

**Thermodynamic Phase And  
Chemical Equilibrium At 0-110°C  
For The  $H^+$  - $K^+$  - $Na^+$  - $Cl^-$  - $H_2O$   
System Up To 16 Molal And The  
 $HNO_3$ - $H_2O$  System Up To 20 Molal  
Using An Association-Based  
Pitzer Model Compatible With  
ASPEN Plus**

**T. T. Nichols  
D. D. Taylor**

September 2003

*Idaho National Engineering and Environmental Laboratory  
Bechtel BWXT Idaho, LLC*



**Thermodynamic Phase And Chemical Equilibrium At  
0-110°C For The  $H^+$ - $K^+$ - $Na^+$ - $Cl^-$ - $H_2O$  System Up To 16  
Molal And The  $HNO_3$ - $H_2O$  System Up To 20 Molal  
Using An Association-Based Pitzer Model Compatible  
With ASPEN Plus**

Todd T. Nichols  
Dean D. Taylor

September 2003

Idaho National Engineering and Environmental Laboratory  
High Level Waste Program  
Idaho Falls, Idaho 83415

Prepared for the  
U.S. Department of Energy  
Assistant Secretary for Environmental Management  
Under DOE Idaho Operations Office  
Contract DE-AC07-99ID13727

## ABSTRACT

A status is presented of the parameterization during FY2003 of an association-based Pitzer model to simulate chemical and phase equilibria of acid-chloride-nitrate-mercury aqueous electrolyte systems at 0-100° C within the industry-standard process simulator, ASPEN Plus. Compatibility with ASPEN Plus requires that the Pitzer model used be limited to the third virial coefficient and have the values of  $b$  and  $\alpha_i$  as originally proposed by Pitzer. Two aqueous models for 0-110° C at atmospheric pressure were parameterized in FY03. The model for the aqueous  $\text{H}^+ \text{-K}^+ \text{-Na}^+ \text{-Cl}^-$  system is applicable for 0-16 molal, and the  $\text{HNO}_3 \text{-H}_2\text{O}$  for 0-20 molal. An association-based Pitzer activity coefficient model is combined with Henry's law to predict activity/osmotic coefficient and VLE. The chloride model also predicts KCl and NaCl solubility, while the nitric acid model has the unique capability of predicting extent of dissociation with an average absolute deviation of 1.43%. The association-based approach presented here extends the utility of the molality-based Pitzer model past 6 molal to predict activity/osmotic coefficients up to 16-20 molal. The association-based approach offers the additional benefits of predicting extent of dissociation and of allowing the Pitzer model to be fully utilized in commercial simulators, such as ASPEN Plus, that require accounting for association to implement Henry's law. The Pitzer models presented here provide the chemical process simulation engineer with a superior alternative to the Electrolyte NRTL model that can easily be used in ASPEN Plus.

## EXECUTIVE SUMMARY

A status is presented of the parameterization during FY2003 of an association-based Pitzer model to simulate chemical and phase equilibria of acid-chloride-nitrate-mercury aqueous electrolyte systems. This work was funded by the Laboratory Directed Research and Development (LDRD) program at the Idaho National Engineering and Environmental Laboratory (INEEL). The Pitzer model was originally developed for the 0-6 molal range, so many of the Pitzer parameter values in the literature are not applicable to high ionic-strength, complex mixtures, such as 10 molal SBW. The objective of this project is to obtain association-based parameters for the Pitzer model that will allow practitioners to perform process design involving liquid speciation, vapor-liquid, and solid-liquid equilibria of high ionic-strength, complex, electrolyte mixtures at 0-100° C within any process simulator where Pitzer's model has been implemented (in particular, ASPEN Plus, which has been selected for process modeling at INEEL).

The parameterization of two aqueous models for 0-110° C at atmospheric pressure were performed in FY03. An association-based Pitzer activity coefficient model is combined with Henry's law to predict activity/osmotic coefficient and vapor-liquid equilibrium. The bulk of the work of parameterization involved the qualification of different data types from different researchers, at similar and different temperatures. The model for the aqueous  $\text{H}^+\text{-K}^+\text{-Na}^+\text{-Cl}^-$  system is applicable for 0-16 molal, and the  $\text{HNO}_3\text{-H}_2\text{O}$  for 0-20 molal. Both models are readily usable in ASPEN Plus. The chloride model predicts KCl and NaCl solubility, while the nitric acid model has the unique capability of predicting extent of dissociation with an average absolute deviation of 1.43%.

We are not aware of any other molality-based Pitzer models for aqueous HCl and  $\text{HNO}_3$  in the literature that are applicable to such broad concentration and temperature ranges while simultaneously being compatible with ASPEN Plus (limited to the third virial coefficient and have the values of  $b$  and  $\alpha_i$  as originally proposed by Pitzer). The comparison between predicted and experimental data is summarized in Table 22. The numbers show that predictions deviate more for phase equilibrium than for activity and osmotic coefficients. Given the experimental uncertainties of the data regressed, the deviations listed in Tbl. 22 are acceptable to the practicing process simulation engineer. The parameterizations of the association-based Pitzer model presented here provide the practitioner with a superior alternative to the Electrolyte NRTL model that can be easily used in ASPEN Plus. These parameterizations extend the usability of the Pitzer approach up to 16-20 molal for hydrochloric and nitric acids, volatile acids whose modeling is limited to 6-7 molal using the traditional complete-dissociation Pitzer model.

The equilibrium constants and Pitzer parameters used for the chloride system that were taken from the literature are shown in Table 18, and the those regressed in this work are displayed in Tables 19 and 20. The parameters in Tbls. 18-20 are recommended for 0-110° C and 0-16 molal for chloride systems and 0-20 molal for nitric acid. Indication is given for those cases where the regressed data (this work) or stated applicability (cited reference) are for a different temperature or concentration range.

Clegg & Brimblecombe (1990) used enthalpy, density, and heat capacity data to model the temperature dependency of the activity coefficient of  $\text{HNO}_3$ . Their work supplied important missing "data" without which our parameterization of the association-based Pitzer model for  $\text{HNO}_3$  could not have been performed.

# CONTENTS

<b>ABSTRACT .....</b>	<b>iii</b>
<b>EXECUTIVE SUMMARY .....</b>	<b>iv</b>
<b>INTRODUCTION .....</b>	<b>1</b>
<b>Process Design.....</b>	<b>1</b>
<b>Role Of Modeling.....</b>	<b>2</b>
<b>Thermodynamic Modeling of Non-Ideal Solutions.....</b>	<b>2</b>
<b>Project Objective .....</b>	<b>3</b>
<b>Brief Overview Of Pitzer Ion-Interaction Model.....</b>	<b>3</b>
<b>Electrolyte Nomenclature .....</b>	<b>4</b>
Solid-Liquid Equilibrium Constant .....	5
Liquid Chemical Equilibrium - The Dissociation Constant .....	5
<b>MODEL PARAMETERIZATION .....</b>	<b>7</b>
<b>Chloride System .....</b>	<b>7</b>
Hydrochloric Acid (HCl-H <sub>2</sub> O) .....	7
Activity & Osmotic Coefficient Data.....	7
Regression of Binary Pitzer Parameters.....	9
Predicted Extent of Dissociation and Molal Activity Coefficient of Associated HCl .....	10
Henry's Law Constant .....	11
Potassium Chloride (KCl) .....	12
Sodium Chloride (NaCl).....	13
Chloride Mixtures (H <sup>+</sup> -K <sup>+</sup> -Na <sup>+</sup> -Cl <sup>-</sup> ).....	13
KCl-NaCl-H <sub>2</sub> O (I ≤ 18 m; 0-110° C) .....	14
HCl-KCl-H <sub>2</sub> O and HCl-NaCl-H <sub>2</sub> O .....	14
HCl-KCl-H <sub>2</sub> O: 2 <sup>nd</sup> Iteration .....	14
HCl-KCl-H <sub>2</sub> O: 3 <sup>rd</sup> Iteration .....	15
@25° C.....	15
HCl-NaCl-H <sub>2</sub> O (I ≤ 19 m) .....	15
KCl-HCl-H <sub>2</sub> O (I ≤ 16 m).....	16
HCl-KCl-NaCl-H <sub>2</sub> O (4 m ≤ I ≤ 14 m).....	16
Results .....	16
Temperatures Other Than 25° C .....	17
HCl-NaCl-H <sub>2</sub> O (I ≤ 17.5 m; 0-50° C).....	17
KCl-HCl-H <sub>2</sub> O (I ≤ 17.3 m; 0-50° C).....	17
Art Rather Than Science .....	18
Solubility Extrapolations .....	18
<b>Nitric Acid (HNO<sub>3</sub>-H<sub>2</sub>O) .....</b>	<b>19</b>
Osmotic And Activity Coefficient Data .....	19
Dissociation Data .....	20
Concentration Limit of Model.....	21
Regression of Pitzer Parameters and Equilibrium Constant .....	22
Dissociation Constant (K <sub>D,HNO3</sub> ).....	22
Pitzer Parameters.....	23
Results.....	23
Henry's Law Constant and Vapor-Liquid Equilibrium .....	24
<b>COMPARISON WITH COMPLETE-DISSOCIATION APPROACH .....</b>	<b>26</b>
<b>Comparison With Traditional, Low-Molality, Complete-Dissociation Model.....</b>	<b>26</b>
Hydrochloric Acid.....	26
m ≤ 6 .....	26
Performance of Association-Based Model Over Larger Concentration Range (m ≤ 16).....	26

Nitric Acid.....	26
$m \leq 6$ .....	26
Performance of Association-Based Model Over Larger Concentration Range ( $m \leq 20$ ).....	27
<b>Comparison With Extended Complete-Dissociation Model .....</b>	<b>27</b>
<b>SUMMARY &amp; CONCLUSIONS .....</b>	<b>29</b>
<b>PATH FORWARD .....</b>	<b>32</b>
<b>REFERENCES .....</b>	<b>33</b>
<b>APPENDIX A: HENRY'S LAW FOR ACID GASES IN ASPEN PLUS.....</b>	<b>37</b>
<b>Introduction .....</b>	<b>38</b>
<b>Compatibility With the Reference State Convention of the Pitzer Model .....</b>	<b>38</b>
<b>Relationship To Form Based On Complete Dissociation .....</b>	<b>39</b>

## FIGURES

1. Harned & Owen vs. Akerlof & Teare Activity Coefficient Data For Aqueous HCl.....	41
2. Comparison Of Osmotic Coefficients Calculated From Akerlof & Teare Water Activity Data For Aqueous HCl. ....	42
3. Assessment Of Impact Of High-Molality Activity Coefficient Data Of Cerquetti et al. (1968) On $\lambda_{(HCl, HCl)}$ @70 And 80° C. ....	43
4. Assessment Of Impact Of High-Molality Activity Coefficient Data Of Cerquetti et al. (1968) On $(\lambda_{(HCl, Cl-)} + \lambda_{(HCl, H+)})$ @70 And 80° C. ....	44
5. Comparison Between Regressed HCl Activity Coefficient Data And Model Predictions. ....	45
6. Comparison Between Regressed Osmotic Coefficient Data And Model Predictions .....	46
7. Comparison Between Model Predictions Of HCl Activity Coefficients And Low-Molality Data Not Used To Regress Pitzer Parameters. ....	47
8. Comparison Between Model Predictions Of HCl Activity Coefficients And High-Molality Data Not Used To Regress Pitzer Parameters. ....	48
9. Predicted Extents Of Dissociation Of HCl In Water.....	49
10. Predicted Molal Activity Coefficient Of Associated HCl For HCl-H <sub>2</sub> O System. ....	50
11. Comparison Of Model vs. Data: HCl Partial Pressure For HCl-H <sub>2</sub> O System. ....	51
12. Comparison Of Dissociation-Based Henry's Law Constants For HCl.....	52
13. Recommended Correlation For Dissociation-Based Henry's Law Constant (Eq. [13]) For HCl.....	53
14. Experimental NaCl Solubility: HCl-NaCl-H <sub>2</sub> O @ 25° C.....	54
15. HCl Partial Pressure: HCl-KCl-NaCl-H <sub>2</sub> O System @25° C.....	55
16. Variation From Constancy In The Saturation Ionic Product Of KCl @0° C Using Final Values For $\theta_{H+,K+}$ , $\psi_{H+,K+,Cl-}$ , And $(\lambda_{(HCl, Cl-)} + \lambda_{(HCl, K+)})$ . ....	56
17. Variation From Constancy In The Saturation Ionic Product Of KCl @25° C Using Final Values For $\theta_{H+,K+}$ , $\psi_{H+,K+,Cl-}$ , And $(\lambda_{(HCl, Cl-)} + \lambda_{(HCl, K+)})$ . ....	57
18. Pattern In Deviaiton Of KCl Saturation Ionic Product @25° C Using Initial Values For $\theta_{H+,K+}$ , $\psi_{H+,K+,Cl-}$ , And $(\lambda_{(HCl, Cl-)} + \lambda_{(HCl, K+)})$ . ....	58
19. Comparison Of Osmotic Coefficients Calculated From VLE Data: HNO <sub>3</sub> -H <sub>2</sub> O System @ 25° C.....	59
20. Comparison Of Osmotic Coefficients Calculated From VLE Data: HNO <sub>3</sub> -H <sub>2</sub> O System @ 20° C.....	60
21. Comparison Of HNO <sub>3</sub> Partial Pressure Data Used By Clegg & Brimblecombe (1990): HNO <sub>3</sub> -H <sub>2</sub> O System @25° C.....	61
20. Comparison Of HNO <sub>3</sub> Partial Pressure Data Used By Clegg & Brimblecombe (1990): HNO <sub>3</sub> -H <sub>2</sub> O System @50° C.....	62
23. Nitric Acid Dissociation @25° C.....	63
24. Multi-Temperature Dissociation Data Of Axtmann et al. (1960): HNO <sub>3</sub> -H <sub>2</sub> O System.....	64
25. Comparison Of HNO <sub>3</sub> Activity Coefficient Data @25° C.....	65
26. Isothermal Fit Of $\beta^0_{(H^+, NO_3^-)}$ .....	66

27. Isothermal Fit Of $\psi_{(HNO_3, HNO_3, HNO_3)}$ .....	67
28. Multi-Temperature Extent Of Dissociation Of Aqueous Nitric Acid: Model vs. Data @0, 25, And 70° C... 68	
29. Multi-Temperature Extent Of Dissociation Of Aqueous Nitric Acid: Model vs. Unregressed Data Of Krawetz At 0 & 50° C. ....	69
30. Multi-Temperature Predictions Of HNO <sub>3</sub> Dissociation In Water. ....	70
31. Multi-Temperature Stoichiometric HNO <sub>3</sub> Activity Coefficient In Water: Predictions vs. Regressed Input..	71
32. Osmotic Coefficient For Aqueous HNO <sub>3</sub> @25° C: Model vs. Data.....	72
33. Predicted Osmotic Coefficient For Aqueous HNO <sub>3</sub> vs. Concentration And Temperature.....	73
34. Activity Coefficient Of Associated HNO <sub>3</sub> In Water @25° C. ....	74
35. Multi-Temperature Predictions Of The Activity Coefficient Of Associated HNO <sub>3</sub> In Water.....	75
36. Comparison Of HNO <sub>3</sub> Henry's Law Constants In Aspen Plus Functional Form. ....	76
37. Multi-Temperature HNO <sub>3</sub> Partial Pressure In Aqueous Solution: Predictions vs. Data.....	77
38. Comparison Of Association-Based And Complete-Dissociation Pitzer Models: HCl @25° C. ....	78
39. Comparison Of Association-Based And Complete-Dissociation Pitzer Models: HNO <sub>3</sub> @25° C.....	79
40. Comparison Of Deviations: Association-Based vs. Extended Complete-Dissociation For HCl @25° C.....	80
41. Comparison Of Deviations: Association-Based vs. Extended Complete-Dissociation For HNO <sub>3</sub> @25° C... 81	
42. Deviation Of Complete-Dissociation Pitzer (1991) Parameterization For HNO <sub>3</sub> Data Of Hamer & Wu (1972) @25° C. ....	82

## TABLES

1. HCl Partial Pressure Of Aqueous Hydrochloric Acid Solution At Total Pressure Of 1 Atm.....	83
2. HCl Partial Pressure Of Aqueous Hydrochloric Acid Solution At Total Pressure Of 1 Atm.....	83
3. Activity Coefficient Of HCl: HCl-KCl-H <sub>2</sub> O System @25° C. ....	84
4. Activity Coefficient Of HCl: HCl-NaCl-H <sub>2</sub> O System @25° C.....	86
5. Activity Coefficient Of HCl: HCl-KCl-NaCl-H <sub>2</sub> O System @25° C.....	88
6. KCl Solubility In Aqueous HCl Solution @25° C. ....	89
7. NaCl Solubility In Aqueous HCl Solution @25° C. ....	90
8. KCl & NaCl Solubility In Aqueous HCl Solution @25° C.....	91
9. HCl Partial Pressure: HCl-KCl-NaCl-H <sub>2</sub> O System @25° C.....	91
10. $\gamma_{\pm, st(HCl)}$ In Aqueous Sodium Chloride: 0-50° C (Excluding 25°). ....	92
11. NaCl Solubility In Aqueous Hydrochloric Acid: 0-30° C (Excluding 25°).....	94
12. KCl Solubility In Aqueous HCl Solution @0° C. ....	95
13. $\gamma_{\pm, st(HCl)}$ Of Dilute HCl In Aqueous Potassium Chloride: 0-50° C.....	96
14. Nitric Acid Dissociation Constant.....	99
15. Nitric Acid Dissociation Results & Data.....	100
16. Nitric Acid Osmotic & Activity Coefficients @25° C.....	102
17. Multi-Temperature HNO <sub>3</sub> Partial Pressure @1 Atm. Total Pressure: Model vs. Data.....	104
18. Equilibrium Constants And Pitzer Parameters For Chloride System Taken From Literature.....	105
19. Pitzer Parameters Regressed In This Work.....	106
20. Equilibrium Constants Regressed In This Work.....	107
21. Average Absolute Deviations Of Complete-Dissociation & Association-Based Approaches @25° C. ....	108
22. Summary Of Results: Average Absolute Deviation Between Predicted And Experimental Values.....	109
23. Data Used To Regress Equilibrium Constants & Pitzer Parameters. ....	110
24. Data Used To Validate, But Not Regress, Model Parameters.....	112

# **Thermodynamic Phase And Chemical Equilibrium At 0-110° C For The $\text{H}^+$ - $\text{K}^+$ - $\text{Na}^+$ - $\text{Cl}^-$ - $\text{H}_2\text{O}$ System Up To 16 Molal And The $\text{HNO}_3$ - $\text{H}_2\text{O}$ System Up To 20 Molal Using An Association-Based Pitzer Model Compatible With ASPEN Plus**

## **INTRODUCTION**

The purpose of this document is to provide a status of the parameterization during FY2003 of an association-based Pitzer model to simulate chemical and phase equilibria of acid-chloride-nitrate-mercury aqueous electrolyte systems. This work was funded by the Laboratory Directed Research and Development (LDRD) program.

Besides the contribution to the scientific community such a model would make, the results would have large applicability to the study of the treatment of liquid Sodium-Bearing Waste (SBW) at Idaho National Engineering and Environmental Laboratory (INEEL). Waste management activities at the INEEL and throughout the DOE complex will entail waste retrieval, characterization, treatment, and packaging for disposal, interim storage, transportation, and final disposal. An immediate focus at the INEEL is retrieval, treatment, and packaging of the liquid SBW inventory in the INTEC Tank Farm Facility (TFF) because of the 1995 Settlement Agreement with the State of Idaho. Consequently, the primary focus of model parameterization during FY2003 has been on species of interest to both the scientific community and INEEL.

## ***Process Design***

An essential tool in developing any chemical process is a process flowsheet (FS) and its associated mass balance (MB). The FS/MB describes the expected process performance, based on the assumptions and known facts about the underlying phenomena which occur during the processing steps. Thus, the FS/MB provides the basis for design and operation of the actual processing facility whose design is under consideration.

The main objectives in generating the FS/MB are as follows:

- (a) Identify all input and output streams for the process;
- (b) Track the chemical components in the input streams through the process, partitioning them among the output streams;
- (c) Describe the chemical form(s) of each input component in the output streams (e.g., how much of the Hg in the offgas will be elemental Hg vapor,  $\text{HgCl}_2$  vapor, and solid  $\text{HgO}$  [aerosol], etc.).
- (d) Determine flowrates and physical properties (temperature, density, corrosivity, etc.) of all process streams needed for equipment design.



The above information is used to generate equipment specifications for process unit operations (e.g., required throughputs, separation or reaction efficiencies, temperatures, etc.), and to assess the adequacy of the process relative to the process requirements (e.g., is the concentration of Hg in the stack gas below the regulatory limit). Both these uses of the MB assume that the information provided in items (a)-(d) above is credible. The resulting design will generally lead to a process fraught with problems - operational, regulatory, etc. - if the data are not credible.

## ***Role Of Modeling***

The reason for building a process simulation model in a commercial process simulator is to provide mass balance accounting to support programmatic planning. Modeling of INEEL SBW treatment processes has been done in the past using linked EXCEL spreadsheets which lack a physical properties database. The objective for FY-2003 was to continue the transition away from the spreadsheet-based simulation toward a full-fledged commercial simulation software package with thermodynamic simulation capability based on a compatible physical properties database. This package will be used to perform basic mass and heat balances on individual unit operations and around the entire treatment train. Having an integrated model with a thermodynamic database will increase the ability of INEEL engineers to assess system-wide impacts of changes to individual unit operations. ASPEN Plus has been tentatively chosen as the commercial process simulator to generate the MB for treatment of SBW (Nichols et al., 2001).

## ***Thermodynamic Modeling of Non-Ideal Solutions***

The following design issues in SBW treatment are considered addressable by thermodynamic modeling: (1) concentrations of corrosive species in liquid and gas process streams; (2) concentrations of regulated pollutants in process effluents (gas and liquid) and their associated waste streams (filters, grouted scrub liquor, etc.); and (3) precipitation of insoluble solids from blending of feed streams of differing compositions. To simulate these entities using standard thermodynamic models requires that the activities of species in solution be calculable from the composition, temperature, and pressure of the solution. Due account should be taken of all species in solution which significantly impact the ionic strength and the activities of the species of concern.

Because the solutions of interest (i.e., blended liquids from the TFF and blowdown effluents from scrubbers) will contain many species at high concentrations (and generally at high ionic strengths), it is necessary that models be used that are capable of estimating activity coefficients (for both ionic and molecular species) in such solutions. The estimated ionic strength of post-evaporation SBW in the TFF is 10 molal, major contributors being nitrate (~5 molar), sodium, and hydrogen (both 1-2 molal).

In the last 3-4 decades a number of activity coefficient models for thermodynamic modeling of aqueous chemical solutions have been proposed. The Electrolyte Non-Random Two-Liquid (ENRTL) model of Chen et al. (1982) is a local composition model for the excess Gibbs energy of electrolyte systems that accounts for two contributions, one resulting from long range electrostatic forces between ions and the other from short range forces between all the species.

In our own literature search, however, we have found far more researchers reporting parameter values for the Pitzer ion-interaction model (Pitzer, 1973) for electrolyte systems than those supporting ENRTL. There appears to be a considerable investment by DOE to generate a Pitzer model database (Weber (2000) and Weber et al. (2000) from ORNL, and Felmy and Rai (1999) and Felmy et al.

(2000) from PNNL). Our own preliminary investigations have shown that the Pitzer approach is appreciably superior to that of the ENRTL with respect to modeling the thermodynamics of complex SBW (Nichols & Taylor, 2002).

## ***Project Objective***

The Pitzer model was originally applied to the 0-6 molal range, so many of the Pitzer parameter values in the literature are not applicable to high ionic-strength, complex mixtures, such as 10 molal SBW. The objective of this project is to develop an association-based approach to the Pitzer formalism that will allow process engineers to perform process design involving liquid speciation, vapor-liquid, and solid-liquid equilibria of high ionic-strength, complex, electrolyte mixtures at 0-100° C within the industry-standard process simulator, ASPEN Plus.

## ***Brief Overview Of Pitzer Ion-Interaction Model***

In simple form, the Pitzer model is a representation of the excess Gibbs free energy ( $G^{\text{ex}}$ ) in a solution which uses a virial equation as follows:

$$\frac{G_{\text{ex}}}{w_w RT} = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(i) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} + \dots \quad [1]$$

where:

$w_w$  = kg of water in the solution

$I$  = ionic strength =  $1/2 \sum_i m_i z_i^2$

$m_i$  = molality of solute specie i

$\lambda, \mu$  = virial coefficients

The first term on the right in Eq. [1] represents the empirically-extended form of the Debye-Huckel limiting law for the long range electrostatic forces between ions. The virial coefficient matrices,  $\lambda_{ij}$  and  $\mu_{ijk}$ , are assumed symmetric. The second virial coefficients ( $\lambda_{ij}$ 's) represent short-range interactions in the presence of the solvent between solute particles i and j. The third virial coefficients ( $\mu_{ijk}$ 's) represent similar three-particle interactions. In general, both the  $\lambda$ 's and the  $\mu$ 's are ionic-strength dependent, though in most cases the dependence is weak for the latter. Pitzer derives individual solute activity coefficients by differentiation of the expression for  $G^{\text{ex}}$  given by Eq. [1]. Thus:

$$\ln \gamma_i = \left[ \frac{\partial \left( \frac{G^{\text{ex}}}{w_w RT} \right)}{\partial m_i} \right]_{n_w} = (z_i^2 / 2) f' + 2 \sum_j \lambda_{ij} m_j + (z_i^2 / 2) \sum_j \sum_k \lambda'_{jk} m_j m_k + 3 \sum_j \sum_k \mu_{ijk} m_i m_j m_k + \dots \quad [2]$$

An expression for the osmotic coefficient,  $\phi$ , is obtained similarly by differentiation of  $G^{\text{ex}}$ . In the Pitzer formalism the coefficient terms in the equations for  $G^{\text{ex}}$ ,  $\ln \gamma_i$ , and  $\phi$  are transformed into a set of empirically-determinable coefficients,  $B_{ij}$ ,  $C_{ij}$ ,  $\Phi_{ij}$ , and  $\Psi_{ijk}$  (one set for the  $G^{\text{ex}}$ ,  $\ln \gamma$ , and  $\phi$  equations, respectively). When these coefficients are substituted for  $\lambda$  and  $\mu$  the resulting activity coefficient equation for cation 'M' is:

$$\begin{aligned} \ln \gamma_M = & z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\Phi_{Mc} + \sum_a m_a \Psi_{Mca}) \\ & + \sum_{a < a'} m_a m_{a'} \Psi_{Maa'} + z_M + \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{nM} + \dots \end{aligned} \quad [3]$$

where  $Z = \sum m_i |z_i|$ , and the indices and subscripts have the following meanings:  $c$  refers to cationic terms,  $a$  to anionic terms,  $n$  to molecular solute terms, and  $a < a'$  refers to single counting of terms involving the same two anions.

An analogous equation applies for the activity coefficient of an anion. The coefficients  $B_{ij}$ ,  $C_{ij}$ ,  $\Phi_{ij}$ ,  $\Psi_{ijk}$ , and  $\lambda_{ij}$  in Eq. [3] are represented as explicit functions of the ionic strength and of the ionic charges. The  $B_{ij}$  coefficients are typically expressed as explicit functions of ionic strength involving two (or more) adjustable ' $\beta$ ' constants ( $\beta^{(0)}$ ,  $\beta^{(1)}$ , ...), while the  $C_{ij}$  and  $\lambda_{ij}$  coefficients are treated as simple adjustable parameters. The  $\Phi_{ij}$  and  $\Psi_{ijk}$  coefficients are non-zero only when there are two or more different electrolytes present in the solution, and hence, are referred to as "mixing" terms. The  $\Phi_{ij}$  term is expressed as follows:

$$\Phi_{ij} = \theta_{ij} + {}^E \theta_{ij}(I) \quad [4]$$

and

$$\Phi'_{ij} = I {}^E \theta_{ij}(I)' \quad [5]$$

where  $\theta_{ij}$  arises from short-range interactions and is treated as a constant, and  ${}^E \theta_{ij}(I)$  is assumed to vary with ionic strength and arises from long-range interactions between ions whose charges are of the same sign but of different magnitudes. The  $F$  term of Eq. [3] involves the derivative of  $\phi$ , and thus, the derivative of  $\theta$ , as indicated in Eq. (E).  ${}^E \theta_{ij}(I)$  and  $I {}^E \theta'_{ij}$  are the so-called "unsymmetrical mixing" terms. Symmetrical mixing is used to refer to the case when ions  $i$  and  $j$  have the same charge (both sign and magnitude, i.e.,  $z_i = z_j$ ). For example, the ternary solution HCl-NaCl-H<sub>2</sub>O involves symmetrical mixing because both cations  $H^+$  and  $Na^+$  have a charge of magnitude one. The ternary solution HCl-CaCl<sub>2</sub>-H<sub>2</sub>O, on the other hand, has unsymmetrical mixing because the charges for the two cations  $H^+$  and  $Ca^{+2}$  have different magnitudes, one and two, respectively.

Finally, the  $\Psi_{ijk}$  parameter is used as a "difference" term to account for differences between the empirically-measured activity coefficient values and those predicted from Eqs. [4] & [5] obtained by assuming the  $\Psi$ 's are zero.

This description of the Pitzer model is admittedly cursory, and is provided as an overview and as a contextual introduction of the terminology that is used later in this report. A more complete description of the Pitzer model can be found in Pitzer (1973; 1991).

## *Electrolyte Nomenclature*

Additional nomenclature used in this report is briefly defined below. The mean ionic activity coefficient of an electrolyte is expressed by

$$\gamma_{\pm}^v = \gamma_+^{v+} \gamma_-^{v-},$$

and the mean ionic molality is given by

$$m_{\pm}^v = m_+^{v+} m_-^{v-},$$

where the total number of ions is given by

$$v = v_+ + v_-.$$

If ionization is assumed to be complete, then

$$m_+ = v_+ m_{\pm},$$

$$m_- = v_- m_{\pm},$$

and

$$m_{\pm, \text{st}}^v = (v_+ m)^{v+} (v_- m)^{v-} = (v_+^{v+} v_-^{v-}) m^v$$

where  $m$  is the total (or stoichiometric) molality of the electrolyte. The stoichiometric ionic molality ( $m_{\pm, \text{st}}^v$ ) is the ionic molality of the electrolyte calculated assuming complete dissociation. Activity coefficients  $\gamma_{\pm}$  calculated on the basis of stoichiometric ionic molalities ( $m_{\pm, \text{st}}$ ) rather than mean ionic molalities ( $m_{\pm}$ ) are referred to in this report as stoichiometric activity coefficients (Denbigh, 1981) and are represented by  $\gamma_{\pm, \text{st}}$ . If an associated specie (intermediate ion, neutral molecule or complex ion) is formed by the solute from its simple ions, the relationship between the stoichiometric and mean ionic functions of the solute is (Robinson and Stokes, 1959, pp. 37-39)

$$\gamma_{\pm, \text{st}} m_{\pm, \text{st}} = \gamma_{\pm} m_{\pm}. \quad [6]$$

### Solid-Liquid Equilibrium Constant

One consequence of the simple relationship given by Eq. [6] is that the ion-based solubility product of an electrolyte has the same value regardless of whether stoichiometric or mean ionic functions are used:

$$K_{\text{sp}} = \gamma_{\pm, \text{st}}^v m_{\pm, \text{st}}^v = \gamma_{\pm}^v m_{\pm}^v. \quad [7]$$

Therefore, in this report all electrolyte solid-liquid equilibrium constants will be in terms of the ions (Eq. [7]) rather than neutral species because such constants can be used whether or not the modeler accounts for association.

### Liquid Chemical Equilibrium - The Dissociation Constant

If an aggregate is formed by the electrolyte in solution, and the aggregate is electrically neutral, Eq. [6] simplifies to

$$\gamma_{\pm, \text{st}} = \alpha \gamma_{\pm}$$

where  $\alpha$  represents the fraction of dissociation. The equilibrium is expressed by

$$K_{D,i} = (\gamma_{+} m_{+})^{v_{+}} (\gamma_{-} m_{-})^{v_{-}} / (\gamma_n m_n)^{v_n}, \quad [8]$$

where  $K_{D,i}$  is the thermodynamic dissociation constant of electrolyte  $i$ , and the subscript  $n$  refers to the neutral aggregate. In the case of the univalent electrolytes nitric and hydrochloric acids, Eq. [H] becomes

$$K_{D,HCl} = (\gamma_{H^{+}} \gamma_{Cl^{-}} m_{H^{+}} m_{Cl^{-}}) / (\gamma_{HCl} m_{HCl}) \quad [8a]$$

and

$$K_{D,HNO_3} = (\gamma_{H^{+}} \gamma_{NO_3^{-}} m_{H^{+}} m_{NO_3^{-}}) / (\gamma_{HNO_3} m_{HNO_3}). \quad [8b]$$

## MODEL PARAMETERIZATION

ASPEN Plus uses the following functional form to describe the temperature dependency of equilibrium constants (dissociation, solubility, and Henry's law):

$$\ln(K_D \text{ or } K_{sp} \text{ or } H_i) = A + B/T + C \cdot \ln(T) + D \cdot T, \quad [9]$$

where  $T$  is in degrees Kelvin. The following form is used to describe the temperature dependency of the Pitzer virial coefficients and mixing parameters:

$$f(T) = P_1 + P_2(T - T^{ref}) + P_3\left(\frac{1}{T} - \frac{1}{T^{ref}}\right) + P_4 * \ln\left(\frac{T}{T^{ref}}\right) + P_5(T^2 - (T^{ref})^2), \quad [10]$$

where  $f(T)$  is the Pitzer parameter,  $T^{ref}$  is 298.15 K, and  $T$  is in degrees Kelvin. ASPEN Plus uses Pitzer's original published values for the parameters  $b$  and  $\alpha_l$ . The value of  $\alpha_l$  is 2 for electrolytes when one of the ions is univalent and 1.4 if neither of the ions is univalent, and  $b$  has a value of 1.2 (Aspen Technology, 2001). The parameterization of Eqs. [9] & [10] for the chloride and nitric acid models was performed using the regression program described in Taylor & Nichols (2003).

The coefficients of Eqs. [9] & [10] fitted to equilibrium constants and Pitzer parameters taken from the literature are shown in Table 18. The first number in the cell is the value at 25° C from the cited source when the coefficients for Eq. [10] had to be fitted from the cited source's tabulated values or values calculated from the source's temperature-dependent correlation. In such cases, a comparison of the first number in the cell and the value of  $p_1$  indicates the degree of inconsistency between the ASPEN Plus functional form and the original source at 25° C. The coefficients of Eqs. [9] & [10] fitted to Pitzer parameters and equilibrium constants regressed in this work are listed in Tables 19 & 20, respectively. Data used to regress model parameters is listed in Table 23, and nonregressed data used for additional model validation is displayed in Table 24.

### *Chloride System*

#### **Hydrochloric Acid (HCl-H<sub>2</sub>O)**

##### *Activity & Osmotic Coefficient Data*

Akerlof & Teare (1937) used emf measurements of the cell H<sub>2</sub>/HCl/AgCl/Ag to determine the activity coefficient of hydrochloric acid in 3-16 molal aqueous HCl for 0-50° C. Marsh & McElroy (1985) detected an error in the expression for the temperature dependence of the dielectric constant of water used by Akerlof & Teare (1937) and noted that the activity coefficients calculated by Akerlof & Teare (1937) are slightly lower than those of Harned & Owen (1958) in the overlap region. Additionally, Fritz & Fuget (1956) assert that the vapor pressure data from the *International Critical Tables* (Vol. III, 1928; referred to as "I.C.T." hereafter) used by Akerlof & Teare (1937) to adjust their emf measurements to one atmosphere pressure has appreciable error. Figure 1 displays the overlap region for the data of Akerlof & Teare (1937) and Harned & Owen (1958) at 20° C. There is a small offset (slightly less than 2 %) in the overlap region between 3-4 molal, but the trends appear to be compatible. This small difference between these two data sources in a small overlap region at lower temperatures should not appreciably affect the overall fit for 0-16 m and 0-110 ° C.

The following sources of stoichiometric HCl activity coefficient values were used: Akerlof & Teare (1937) [3-16 m and 0-50° C], Cerquetti et al. (1968) [1-11 m over 25-80° C, and 1 m @90° C], Hamer & Wu (1972) [0-16 m @25° C], Harned & Owen (1958) [0-2 m and 0-50° C], Hawkins (1932)

[1-4 m @25° C], Holmes et al. (1987) [0-7 m at 90-110° C], Macaskill et al. (1977) [emf data for  $m \leq 1$  and 5-45° C], Partanen & Covington (2002) [0.01 m over 0-60° C], and Robinson & Stokes (1959) [0-6 m @25° C].

As previously noted, Fritz & Fuget (1956) assert that the HCl partial pressure data from the I.C.T. in the temperature range 0-50° C is very inaccurate. They claim that below 5 molal, the I.C.T. values range from 10% high at 4 molal to 100% high at 0.5 molal. They also state that above 11 molal the values are 5-20% high, with the error decreasing with increasing temperature. Between 6 and 11 molal, Fritz & Fuget (1956) found that theirs and the I.C.T. HCl partial pressure data agreed to within 5%. The I.C.T. water partial pressure data was found to be uniformly 3-5% too low at 0-50° C. Carslaw et al. (1995), in their parameterization of a Pitzer mole-fraction based model for HCl, confirmed the inconsistency of the I.C.T. vapor-liquid equilibrium (VLE) data at 25° C. They also confirmed the slight systematic difference between the activity coefficient data of Akerlof & Teare (1937) and Harned & Owen (1958), but Carslaw et al. (1995) concluded that this activity coefficient discontinuity, although apparent at all temperatures involved, did not appreciably affect the overall fit of their model.

Past 50° C, the amount of experimental HCl activity/osmotic coefficient data in the literature decreases. Data for greater than 11 molal doesn't exist past 50° C, and the data at temperatures higher than 80° C appears to be confined to the 0-1 molal range. Consequently, model predictions of Holmes et al. (1987) and water partial pressure data of the I.C.T. were used to fill in the data gaps above 50° C.

Holmes et al. (1987) used enthalpy of dilution, heat capacity, activity coefficient, and osmotic coefficient data to produce a comprehensive model of the thermodynamics of HCl up to 648 K and 40 MPa. They concluded that the Pitzer approach, assuming complete dissociation, required a fourth virial coefficient for accurate predictions above 7 molal. Model I of Holmes et al. (1987), the traditional Pitzer approach using three virial coefficients, was used by us to estimate activity and osmotic coefficients in the 0-7 molal range at 90, 100, and 110° C.

For higher molalities, the water partial pressure data of I.C.T., as given in the chemical engineering handbook of Perry & Green (1997), was used to estimate the osmotic coefficient. We made the common assumption that the gas phase behavior is ideal and calculated the water activity from

$$a_w = \frac{p_w}{p_w^o}, \quad [11]$$

and the stoichiometric molal osmotic coefficient from

$$\ln a_w = \frac{-M_w \phi_{st} 2m}{1000}, \quad [12]$$

where  $a_w$  is the activity of water,  $p_w$  is the partial pressure of water,  $p_w^o$  is the vapor pressure of pure water at the system temperature,  $M_w$  is the molecular weight of water, and  $m$  is the stoichiometric molality of the univalent solute (HCl in this case). One has to be cautious when using water partial pressures of aqueous binary solutions when the solute is also volatile to estimate osmotic coefficients because of inconsistencies in VLE data (see the discussion on HNO<sub>3</sub> and the paragraph below regarding the Akerlof & Teare data). Fritz & Fuget (1956) did not assess the I.C.T. vapor pressure data above 50° C, but the error below 50° C was relatively small for the partial pressure of water (3-5 % error). Consequently, osmotic coefficients calculated from the I.C.T. water partial pressure data in the 8.7-16.8 molal range at 60-110° C were used as "data" because they appeared to be smooth functions and reasonably compatible with the lower-molality predictions of Model I of Holmes et al.

(1987). In this way, activity/osmotic coefficient estimates were obtained for the entire concentration and temperature ranges of interest (0-16 molal and 0-110° C, respectively).

Akerlof & Teare (1937) used their multiparameter correlation for the activity coefficient of HCl with the Gibbs-Duhem equation to predict the activity of water over 3-16 m and 0-50° C, from which we calculated stoichiometric osmotic coefficients (Eq. [12]). The resulting osmotic coefficients, however, were appreciably inconsistent with the results of other researchers. This can be seen from Figure 2. Not only does the Akerlof & Teare data at 0° C not smoothly approach that of Holmes et al. (1987), its 0° C trend would appear to extrapolate at lower concentrations to values even lower than the 75° C data of Holmes et al. (1987). Nor do the osmotic coefficients of the Akerlof & Teare water activity data at 20° and 30° C envelop the 25° C values of Hamer & Wu (1972). Consequently, the water activity data of Akerlof & Teare (1937) was not used in the regressions. Only the limited osmotic coefficient data of Hamer & Wu (1972) [0-16 m @25° C] and Robinson & Stokes (1959) [0-6 m @25° C], the predictions of Holmes et al. (1987) [0-7 m at 90-110° C], and the water partial pressures of I.C.T. [8.6-16.8 m at 60-110° C] were used to estimate stoichiometric osmotic coefficients in the regressions.

### ***Regression of Binary Pitzer Parameters***

Although hydrochloric acid in aqueous solution is considered mostly dissociated at temperatures under 250° C (Simonson et al., 1990; Holmes et al., 1987), one has to account for association when modeling HCl in ASPEN Plus because the Henry's law formalism of the software is in terms of neutral species rather than ions (see Appendix A). Simonson et al. (1990) showed that different values of a dissociation constant, several orders of magnitude apart, can fit excess thermodynamic data equally well when the extent of dissociation is known to be high. Although the predicted speciation may be different, activity and osmotic coefficients, for example, may be reproduced with similar accuracy. Because it is estimated that association of hydrochloric acid is minimal below 250° C, a firm value of the equilibrium constant and exact knowledge of speciation, therefore, are not critical for our target temperature range. What is required in our case is a model that will predict reasonable trends in the quantitatively-small association with respect to concentration and temperature such that Henry's law can be utilized to predict partial pressures of associated HCl in ASPEN Plus while simultaneously reproducing stoichiometric activity/osmotic coefficient data. Consequently, the values of the equilibrium constant estimated by Robinson (1936) for 0°-50° C were arbitrarily selected for the basis of a correlation for the dissociation constant. The points at 30°, 40°, and 50° C were used to extrapolate to 100° via the van't Hoff expression. Eleven points between 0 and 100° C were then used to regress the four coefficients of ASPEN Plus' functional form for the equilibrium constant.

In preliminary regressions at 25° C, the activity coefficient of the associated acid was assumed equal to one and only the binary ion-ion interaction parameters were used, which resulted in acceptable agreement with the activity and osmotic coefficient data. However, the neutral species interaction parameters  $\lambda_{(\text{HCl}, \text{HCl})}$  and  $(\lambda_{(\text{HCl}, \text{Cl}^-)} + \lambda_{(\text{HCl}, \text{H}^+)})$  were added to the model because their inclusion reduced the absolute % deviation of the hydrochloric acid partial pressure predictions by half without increasing the error in the activity and osmotic coefficient predictions. We choose to give values of the neutral-ion interaction terms ( $\lambda_{n,i}$ ) as sums of neutral combinations because it is only the sums that are determinable. The user can then select one ion for which to set the neutral-ion interaction term to zero when implementing the Pitzer model.

The subsequent addition of  $\mu_{(\text{HCl}, \text{HCl}, \text{HCl})}$  at 25° C further reduced the error in the partial pressure predictions by almost one third, but at the expense of the accuracy of the activity and osmotic coefficient predictions. Consequently, this ternary interaction term was not included in the model.

Isothermal regressions of the five binary Pitzer parameters from activity/osmotic coefficient data were performed at 25° C and at ten-degree intervals over the range 0-110° C. The resulting



parameter values were plotted with respect to temperature. The three values for  $C^\phi$  at 60-80° C, magnitude and sign, were not consistent with the values at the other temperatures. The magnitude of all the  $C^\phi$  values was small, and the temperature plot had an overall negative slope. Consequently, two approaches were tried. In one, the value of  $C^\phi$  was set to zero at all temperatures. In the other, a linear correlation was regressed for  $C^\phi$  excluding the 60-80° points. The isothermal regressions of the other Pitzer parameters were repeated in each of the two approaches. The simple linearization was adopted because it resulted in slightly better fits of the activity/osmotic coefficient data in the isothermal regressions than did setting  $C^\phi$  to zero.

Using the linear correlation for  $C^\phi$ , the subsequent temperature plots of  $\beta^{(0)}$  and  $\beta^{(1)}$  were fairly linear, so they too were linearized, and the isothermal regressions were again repeated for the remaining two parameters,  $\lambda_{(\text{HCl}, \text{HCl})}$  and  $(\lambda_{(\text{HCl}, \text{Cl}^-)} + \lambda_{(\text{HCl}, \text{H}^+)})$ . These two parameters deviated from their respective general trends at 70 and 80° C. Holmes et al. (1987) noted that the activity coefficient data of Cerquetti et al. (1968) deviated at high molalities from the predictions of their model, the highest deviation occurring at 80° C. We noted that the data of Cerquetti et al. (1968) were consistently lower than the predictions of our isothermal parameterizations at  $T \geq 40^\circ \text{C}$  and stoichiometric concentrations greater than 7 molal, with the deviations increasing with increasing temperature. Consequently, the weighting factor for the activity coefficient data of Cerquetti et al. (1968) at  $m > 7$  molal was set to zero at 70 and 80° C, and the isothermal regressions were repeated at these two temperatures. The resulting isothermal values for  $\lambda_{(\text{HCl}, \text{HCl})}$  and  $(\lambda_{(\text{HCl}, \text{Cl}^-)} + \lambda_{(\text{HCl}, \text{H}^+)})$  at 70 and 80° C fell nicely onto the general temperature trends formed by their respective values at other temperatures. Figures 3 & 4 show the improved consistency resulting from not using the high-molality data of Cerquetti et al. (1968) at 70 and 80° C. The improved set of values were used in the final temperature curve fitting of  $\lambda_{(\text{HCl}, \text{HCl})}$  and  $(\lambda_{(\text{HCl}, \text{Cl}^-)} + \lambda_{(\text{HCl}, \text{H}^+)})$  to the full, 5-coefficient functional form of ASPEN Plus.

The comparison between the activity and osmotic coefficient data used in the regression and the predictions of our parameterization is displayed in Figures 5 & 6, respectively. The agreement is very good - an average absolute deviation of 0.6% for activity coefficient and 0.3% for osmotic coefficient. Deviation, or residual, is in terms of (data - predicted)/data. The variation in residual for osmotic coefficient, however, is greater than for the activity coefficient because of the inherent error in the VLE data used to estimate the osmotic coefficients at high molalities and high temperatures. The average absolute deviation of the predictions from the osmotic coefficients calculated from the I.C.T. water partial pressure data at 6-16.8 m and 60° C, for example, is 1.4%, which is consistent with the assumed 3-5% error of the water partial pressure data.

Agreement with low-molality activity coefficient data not used in the regression is also very good - an average absolute deviation of 0.24 % for the data of Harned & Owen (1958), Macaskill et al. (1977), and Partanen & Covington (2002) at 5, 15, 35, 45, and 55° C (see Figure 7). Figure 8 shows the relatively poor agreement between our parameterization of the Pitzer model and the high-molality data of Cerquetti et al. (1968) at 70 and 80° C that was excluded from the regressions. The average deviation of the eight data points is -4.5%. The largest deviation of -12% occurred at 80° C and 11.1 molal, compared to the -6% maximum difference noted by Holmes et al. (1987) with their parameterization.

#### Predicted Extent of Dissociation and Molal Activity Coefficient of Associated HCl

The predicted extent of dissociation with respect to concentration and temperature is displayed in Figure 9. The model predictions agree with the assertion of other researchers that the association of hydrochloric acid is minimal in our target concentration and temperature ranges.

The predicted molal activity coefficient of associated molecular HCl is displayed in Figure 10. The values are mostly below one at the lower temperatures, and the activity coefficient vs. concentration curve doesn't become monotonically increasing from a value of one at infinite dilution until 90° C. The trend of the activity coefficient increasing with increasing temperature at a given concentration is the reverse of the trend for nitric acid (see Fig. 35).

Interestingly, the inclusion of  $\mu_{(\text{HCl}, \text{HCl}, \text{HCl})}$  at 25° C in the preliminary regressions caused the values of the activity coefficient of the associated acid to be larger - closer to one at dilute concentrations and above one at higher concentrations. It was mentioned earlier, however, that the inclusion of  $\mu_{(\text{HCl}, \text{HCl}, \text{HCl})}$  at 25° C in the preliminary regressions decreased the accuracy of the activity and osmotic coefficient predictions and was consequently dropped from the model. Without extent of dissociation data and/or a reliable value of the dissociation constant, the stoichiometric molal activity and osmotic coefficient data do not constrain the thermodynamics enough to accurately determine dissociation and activity coefficient of the associated acid. Figs. 9 and 10 are given, therefore, not as validated representations of reality but as possibilities and to give insight into the predictive thermodynamic nature of our parameterization of the Pitzer model.

### ***Henry's Law Constant***

Fritz & Fuget (1956) did not assess the I.C.T. vapor pressure data above 50° C, but we assume that the HCl partial pressure data between 6 and 11 molal in the 60-110° C range has similar accuracy as determined for the 0-50° C range ( $\pm 5\%$ ) and that the trend of decreasing deviation with increasing temperature for > 11 molal continues past 50° C. Consequently, the HCl partial pressure data of I.C.T. at >6 molal and 60-110° C was combined with that of Fritz & Fuget (1956) at 0-15.9 molal and 0-50° C to regress the temperature coefficients of the Henry's law constant, using the correlations for the equilibrium constant and the Pitzer parameters previously determined. The resulting parameterization reproduces the regressed data very well (average absolute deviation of 2.7% over a span of 12 orders of magnitude in HCl partial pressure), as can be see in Figure 11. Some high-temperature ( $T > 50^\circ \text{C}$ ) data below 6 molal that was not used in the regression is also displayed in Fig. 11, and one can see that the model under predicts those points. This under prediction is consistent with the known systematic error of the I.C.T low-temperature data.

As additional validation of the model's VLE predictive capability, a comparison of the model predictions with the boiling point data of Sako et al. (1984) at one atmosphere total pressure and the total pressure vs. boiling temperature of Sako et al. (1985) are shown in Tables 1 & 2, respectively. For the data at one atmosphere total pressure, one can see from Table 1 that the model appreciably under predicts the data below 6 molal, similar to the I.C.T. data. Assuming the gas phase is ideal and using Eqs. [11] & [12], the first data point of Sako et al. (1984) at 101.05° C and 1.26 molal corresponds to an osmotic coefficient of 0.86, which is about 15% lower than what our parameterization and Model I of Holmes et al. (1987) predict. Perhaps the Sako et al. (1984) data has a systematic error at low molalities similar to that of I.C.T.

In Table 2 is compared the total pressure data of Sako et al. (1985) for aqueous HCl (partial pressure data is not given), the predictions of our parameterization of the Pitzer model, and the predictions of an ENRTL model of Luckas & Eden (1995) proposed for 0-15 molal and 0-100° C. Luckas & Eden (1995) regressed a Henry's law constant to HCl partial pressure data at 0-50° C, and then concluded that their model was accurate up to 121° C solely based upon the agreement between their model and the *total pressure* data of Sako et al. (1985). However, one can see a few cases in Table 2 where the percent deviation from the total pressure data is small for both models, but the predicted HCl partial pressures from the two models are appreciably different, - as high as 29.5% different at 6.6 molal and 121° C. Consequently, one needs to be cautious before asserting accuracy of a VLE model based solely on apparent agreement with an aggregate variable such as total pressure. Our model has an average absolute % deviation of 1.36% from the data.

Carslaw et al. (1995) used enthalpy of dilution, partial molar heat capacity, emf, VLE, and freezing point data to parameterize a mole-fraction activity coefficient model and corresponding Henry's law constant applicable for -93 to 60° C, assuming complete dissociation of the acid. Using Eq. A9 of Appendix A and our assumed correlation for the dissociation constant, values of the Henry's law constant based on complete dissociation and stoichiometric ionic molalities rather than the associated species are calculated. They are compared with the values of Carslaw et al. (1995) at 10° increments in Figure 12. One can see that the Henry's law constant in the complete-dissociation form of Carslaw et al. (1995) calculated from our parameterized model is consistent with that of Carslaw et al. (1995) themselves. For the applicable overlap range of the two models, 0-60° C, the average absolute deviation between the two is only 0.8%. Values from Carslaw et al. (1995) for -90 to -10° C, the average of both models for 0 - 60° C, and the values from our model for 70 - 110° C were used to develop the following correlation for the complete-dissociation Henry's law constant (defined by Eq. [A7]) applicable for -90 to 110° C:

$$\ln(H_{HCl}^d) = 357.4334 - \frac{3129.6252}{T} - 62.0944 * \ln(T) + 0.071717 * T, \quad [13]$$

where T is in degrees Kelvin. The above correlation is recommended for those whose modeling conditions and/or software environment are amendable to ignoring association. The correlation is plotted in Figure 13.

The parameterization of the association-based Pitzer model and Henry's law for HCl proposed in this work are valid for 0-16 molal and 0-110° C at saturation or atmospheric pressures and are readily usable in ASPEN Plus. The model is consistent with the activity/osmotic coefficient predictions of the high-temperature, high-pressure, moderate-concentration parameterization of Model I of Holmes et al. (1987) and the low-temperature correlation of the Henry's law constant of Carslaw et al. (1995).

We are not aware of any other molality-based Pitzer model for aqueous HCl in the literature that is applicable to such broad concentration and temperature ranges and is limited to only the third virial coefficient and has the values of  $b$  and  $\alpha_i$  as originally proposed by Pitzer. The Pitzer-based, ion association-interaction model of Simonson et al. ((1990) uses only up to the third virial coefficient and is applicable to much larger temperature and pressure ranges, but it is limited to 0-2 molal. The parameterizations of Model II and Model III of Holmes et al. (1987), although applicable to much larger temperature and pressure ranges for 0-16 molal, requires a fourth virial coefficient or a temperature-dependent value of  $\alpha_2$ , respectively, and are therefore not readily usable in ASPEN Plus. Perez-Villasenor et al. (2002) have developed a Pitzer model framework for 25° C and up to 25 molal for univalent electrolytes, but their value of  $\alpha_i$  is zero, and their values of  $b$  are regressed and are electrolyte-dependent. A floating value for  $b$  and a universal value of zero for  $\alpha_i$  are not compatible with the current implementation of the Pitzer model in ASPEN Plus.

### Potassium Chloride (KCl)

Complete dissociation was assumed for this salt. Conceicao et al.(1983) report the mean molal activity coefficients at saturation for KCl from 10 to 300° C using the binary Pitzer parameters for KCl determined by Holmes & Mesmer (1983) from isopiestic and vapor pressure measurements, electrochemical cell potentials, freezing temperature determinations, enthalpies of solution and dilution, and heat capacities. Conceicao et al.(1983) validated the Pitzer parameter values with solubility data in a manner similar to that which Pitzer et al. (1984) did for NaCl. These experimental saturation molalities and the corresponding predicted activity coefficients for 10-120° C ( $4.2 \leq m_{\text{sat}} \leq 8.0$ ) were used by us to calculate the thermodynamic solubility product for KCl at several temperatures. The coefficients for the temperature-dependent correlation for the solubility product (Eq. [9]) were then regressed.

The value of the solubility product at 25° C is 8.08, which is consistent with values from the literature - 7.50, 7.91, 7.93, 8.55, and 8.08 (Weber (2000), Sillen & Martell (1971), Christov (2001), Sillen & Martell (1971), and Lu et al. (1996), respectively). However, one can not assume agreement between temperature-dependent correlations of different researchers/models based merely on agreement at one temperature. For example, the solubility product from the model of Lu et al. (1996) is appreciably different than ours at temperatures other than 25° C despite having the same value of 8.08 at room temperature. The solubility product of the solvation-based model of Lu et al. (1996) changes almost five orders of magnitude over the temperature range 0-100° C, from a value of 0.6 at 0° C to  $1.1775 \times 10^4$  at 100° C, compared to our parameterization of the Pitzer model that gives a value of 4.3 at 0° C and 22.1 at 100° C.

The ASPEN-Plus temperature-dependent coefficients for the binary parameters (Eq. [10]) were regressed from the temperature-dependent correlation given by Greenberg & Moller (1989) for 0-250° C and  $I \leq 18$  m. The correlations of Greenberg & Moller (1989) were assessed by comparing predictions with the following activity/osmotic coefficient data for the KCl-H<sub>2</sub>O system: Robinson & Stokes (1959) and Hamer & Wu (1972) at 25° C, Harned & Owen (1958, pg. 727) at 0-40° C, Hellams et al. (1965) at 45° C, Humphries et al. (1968) at 60° C, Moore et al. (1972) and the data of Snipes et al (1975; as given by Zemaitis et al., 1986, pg. 138) at 80° C, and Holmes et al. (1978) at 109° C. There was good agreement. There is appreciable variability in the data at 25° C, reflecting differences between different researchers in methods, assumptions, and models used to collect and interpret the data.

The ASPEN-Plus temperature-dependent correlations for the binary Pitzer parameters transformed from Greenberg & Moller (1989) and the solubility product were then used with other multi-electrolyte solutions in equilibrium with solid potassium chloride to regress mixing parameters for HCl-KCl interactions.

### **Sodium Chloride (NaCl)**

Complete dissociation is assumed for this salt. Pitzer et al. (1984) performed an extensive analysis of the thermodynamic properties of sodium chloride for 273 - 573 K. They used experimental measurements of osmotic/activity coefficients, enthalpy, and heat capacity to regress the Pitzer binary parameters for sodium chloride. We fitted the ASPEN-Plus temperature-dependent coefficients for the binary parameters from their recommended values of the binary parameters given for 0-100° C.

The solubility data of NaCl in water of other researchers were used by Pitzer et al. (1984) to assess the validity of their parameterization of the Pitzer model. We used these experimental saturation molalities of NaCl in water and the corresponding activity coefficients predicted from their parameterization to calculate the thermodynamic solubility product for NaCl at several temperatures. The coefficients for the ASPEN-Plus temperature-dependent correlation for the solubility product were then regressed. The value at 25° C is 38.18, which is consistent with values from the literature - 35.73, 37.17, and 37.19 (Weber (2000), Sillen & Martell (1971), and Lu et al. (1996), respectively). Again however, the solubility product from the model of Lu et al. (1996) is appreciably different than ours at temperatures other than 25° C. The solubility product of the solvation-based model of Lu et al. (1996) changes four orders of magnitude over the temperature range 0-100° C, from 5.2 at 0° C to  $1.1474 \times 10^4$  at 100° C, compared to our parameterization of the Pitzer model that is parabolic and gives a value of 31.5 at 0° C and 37.8 at 100° C.

The temperature-dependent correlations for the solubility product and binary parameters were then used with other multi-electrolyte solutions in equilibrium with solid sodium chloride to regress mixing parameters for HCl-NaCl interactions.

### **Chloride Mixtures (H<sup>+</sup>-K<sup>+</sup>-Na<sup>+</sup>-Cl<sup>-</sup>)**

### ***KCl-NaCl-H<sub>2</sub>O ( $I \leq 18$ m; 0-110° C)***

Since both sodium and potassium chloride are being treated as completely dissociated in our parameterization of the Pitzer model, the temperature-dependent correlation for the mixing parameters were taken from Greenberg & Moller (1989), applicable to 0-250° C and  $I \leq 18$  m. The osmotic coefficient data of Dinane et al. (2002) @25° C and the multi-temperature solubility data of Linke & Seidell (1965, pp. 146-148), Conceicao et al. (1983), and Sterner et al. (1988), covering the ionic strength range 0.2-9.4 m, were used to assess the reliability of these Pitzer mixing parameters for KCl-NaCl, and the predictions compare favorably with the data.

### ***HCl-KCl-H<sub>2</sub>O and HCl-NaCl-H<sub>2</sub>O***

Applicable data is available only for the temperature range 0-50° C, so a simple inverse relationship with temperature was assumed for the mixing and neutral-ion parameters for each ternary system to facilitate extrapolation to higher temperatures. Researchers commonly assume linearity over large temperature ranges for mixing parameters (Conceicao et al., 1983; Greenberg & Moller, 1989).

Activity/osmotic coefficient and solid-liquid equilibrium (SLE) data at 25° C for HCl-KCl-H<sub>2</sub>O, HCl-NaCl-H<sub>2</sub>O, and HCl-KCl-NaCl-H<sub>2</sub>O were used to regress simultaneously all remaining Pitzer parameters (except for KCl-NaCl interactions, which are from Greenberg & Moller, 1989) for the quaternary system at 25° C. The resulting pertinent parameter values for each ternary system at 25° C were then assessed with respect to the multi-temperature data for each ternary system. In the case of the ternary system HCl-NaCl-H<sub>2</sub>O, the parameters from the global simultaneous regression at 25° C fit relatively smoothly with the values at other temperatures and did not need to be changed.

#### **HCl-KCl-H<sub>2</sub>O: 2<sup>nd</sup> Iteration**

The HCl-KCl-H<sub>2</sub>O system, however, posed some problems. There is only solubility data at 0 and 25° C. The HCl activity coefficient data of Harned & Owen (1958) for 0-50° C for solutions dilute in HCl were predicted too high when the ternary  $P_1$  coefficients of Eq. [10] were held to their value from the global simultaneous regression at 25° C. The molarity of hydrochloric acid was constant at 0.01 while the molality of KCl ranged from 0 to 3.5 m. The deviation of the predicted values increased with increasing temperature and increasing potassium chloride concentration. The error was negligible at 0°, but at the highest KCl concentration of 3.5 m the predictions were 4-5% too high at 25° and about 15% at 50° C.

It was desired to maintain equal weighting between the activity coefficient (dilute) and solubility (concentrated) data in order to maintain a balance of the model's predictive capability between dilute and concentrated solution thermodynamics. Consequently, isothermal parameter regressions were performed of the ternary data. The lamda parameter ( $\lambda_{(HCl, Cl^-)} + \lambda_{(HCl, K^+)}$ ) was set equal to zero at temperatures lacking solubility data because the concentration of associated HCl can be assumed to be negligible in the dilute solutions corresponding to the Harned & Owen (1958) activity coefficient data. The mixing parameter theta appeared relatively linear, so it was linearized with respect to the inverse of temperature using all the isotherms. Isothermal regressions were repeated to obtain new values for psi and lamda. Lamda, ( $\lambda_{(HCl, Cl^-)} + \lambda_{(HCl, K^+)}$ ), was then linearized from the only two applicable isothermal regressions - 0 and 25° C. Psi had a general upward trend with respect to temperature, but there was appreciable scatter in the isothermal values, especially at 25° C due to the solubility data. Linearizing psi using all the isotherms resulted in unacceptably poor predictions for solubility. Consequently, psi was linearized using just the two values at 0 and 25° C to capture the concentration dependency that the solubility data at those two temperatures offered.

One could obtain a better fit of the multi-temperature ternary data between 0 and 50° C by allowing psi to depend nonlinearly on temperature, but that resulted in a decreasing value of psi with

increasing temperature at  $T > 50^\circ \text{C}$ , which is the inverse of the overall general upward trend of the isothermal values. This fact, coupled with the fact that  $\psi$  is commonly determined to be linear by other researchers in the literature, caused us to feel that the value of  $\psi$  and the confidence of the model's predictive capacity for concentrated solution would be suspect past  $50^\circ \text{C}$  if the nonlinear form was used for  $\psi$ . Consequently, using activity coefficient and solubility data at two temperatures to linearize  $\psi$  and  $(\lambda_{(\text{HCl}, \text{Cl}^-)} + \lambda_{(\text{HCl}, \text{K}^+)})$  seemed to provide a better balance between dilute/concentrated and parameter stability/predictive accuracy.

The procedure described above resulted in an appreciable reduction in the predicted deviation of the activity coefficient data at temperatures greater than  $25^\circ \text{C}$  - the deviation for 3.5 m at  $50^\circ \text{C}$  was almost cut in half to 7.9% - while loosing some accuracy for the ternary solubility data at  $0^\circ \text{C}$  but loosing no accuracy for solubility at  $25^\circ \text{C}$ . The main cost was in less predictive capability for the quaternary mixture at  $25^\circ \text{C}$  - 2.5% error increased to 3.1% for the HCl activity coefficient, 6.3% error increased slightly to 6.6% for NaCl saturation, and 4.3% error for KCl saturation increased to 5.5%. Interestingly, the deviation of the model for HCl partial pressure data over HCl-KCl-NaCl-H<sub>2</sub>O mixtures at  $25^\circ \text{C}$  *decreased* from 7.4% to 5.6%.

As further validation of the parameters for HCl-KCl aqueous mixtures, predictions of the stoichiometric activity coefficient of HCl in such mixtures from 0 to  $45^\circ \text{C}$ , ionic strengths up to 1.5 m, and KCl ionic strength fractions from 0.1 to 0.9 were compared with values calculated from the emf data of Macaskill et al. (1978). The average absolute deviation was 0.60%, but the trend with temperature was opposite that of the regressed data of Harned & Owen (1958) - the absolute deviation *decreased* with increasing temperature (from 0.66% at  $5^\circ \text{C}$  to 0.54% at  $45^\circ \text{C}$ ).

The average absolute deviation for all HCl stoichiometric activity coefficient data, regressed and nonregressed, for 0- $50^\circ \text{C}$  was 0.88%. The average absolute deviation for all regressed KCl solubility data in the ternary system at 0 and  $50^\circ \text{C}$  was 4.34%.

### HCl-KCl-H<sub>2</sub>O: 3<sup>rd</sup> Iteration

The emf data of Macaskill et al. (1978) was included in the activity coefficient data set for new isothermal regressions performed at 5-degree intervals between 0 and  $50^\circ \text{C}$ . The linear relationship for  $(\lambda_{(\text{HCl}, \text{Cl}^-)} + \lambda_{(\text{HCl}, \text{K}^+)})$  that was determined in the previous second iteration was kept, fixing the values of this Pitzer parameter. The mixing term  $\theta$  was then linearized because it appeared to be more linear than  $\psi$ . New isothermal regressions were performed, from which  $\psi$  was then linearized. The result was improvement in the predictive capacity for HCl stoichiometric activity coefficient (average absolute deviation decreased from 0.88 to 0.45%) but appreciable loss of predictive capacity for KCl precipitation (average absolute deviation increased from 4.34 to 21.30%). Consequently, the parameter set from the 2<sup>nd</sup> iteration is deemed superior, and they are included in the parameter listing given in Tbl. 19.

The data, model comparisons, and procedure pertaining to the regression of mixing parameters for the chloride systems are described in more detail below.

### @ $25^\circ \text{C}$

#### HCl-NaCl-H<sub>2</sub>O ( $I \leq 19 \text{ m}$ )

The solubility of NaCl over the ionic strength range 6-19 m (Linke & Seidell, 1965, pp. 962-963) and the activity coefficient of HCl over the ionic strength range 0.02-7.0 m (Harned & Owen,

1958; Hawkins, 1932; Macaskill et al., 1977 [emf data]; and Jiang, 1996a), all pertaining to the HCl-NaCl-H<sub>2</sub>O system at 25° C, were used to provide ternary data applicable to  $I \leq 19$  m.

#### KCl-HCl-H<sub>2</sub>O ( $I \leq 16$ m)

The solubility of KCl over the ionic strength range 5-16 m (Linke & Seidell, 1965, pp. 962-963) and the activity coefficient of HCl over the ionic strength range 0.01-5.0 m (Harned & Owen, 1958; Hawkins, 1932; and Macaskill & Bates, 1978 [emf data]), all pertaining to the HCl-KCl-H<sub>2</sub>O system at 25° C, were used to provide ternary data applicable to  $I \leq 16$  m.

#### HCl-KCl-NaCl-H<sub>2</sub>O ( $4 \text{ m} \leq I \leq 14 \text{ m}$ )

HCl activity coefficient (Jiang, 1996b) and solubility (Linke & Seidell, 1965, pp. 146-148) data for the quaternary system, ionic strength ranges of 4-6 m and 7-14 m, respectively, were also used.

### Results

Experimental data and predictions from the parameterized chloride model for activity coefficients and solubility are compared in Tables 3-5 and 6-8, respectively. Note that in Table 5 the % deviation, rather than the % absolute deviation, is displayed, but all the values are positive. The model under predicts the HCl stoichiometric molal activity coefficient in all cases for the quaternary mixture relative to the data of Jiang (1996b), with the deviation increasing with increasing stoichiometric ionic strength and increasing KCl ionic strength fraction. One can see from Tbl. 4 that the model also under predicts the HCl activity coefficient data of Jiang (1966a) for the HCl-NaCl-H<sub>2</sub>O ternary system. It appears that our parameterization of the chloride model has a downward bias for the stoichiometric HCl molal activity coefficient in the presence of NaCl with respect to the data of Jiang (1996a-b).

Table 6 shows the solubility results for KCl in aqueous HCl. The last row was not used to regress parameters but is displayed to show that the parameterization extrapolates well. Table 7 displays the information for the solubility of sodium chloride in aqueous hydrochloric acid solutions. The predictions match the data very well for all but two points - NaCl saturation concentrations of 5.94 and 11.5 m. At these two points, the predicted ionic product is 9.6 and 21.4% higher than the solubility product, respectively, which means the parameterization predicts lower NaCl saturation concentrations than the experimental data. The experimental solubility data for the HCl-NaCl-H<sub>2</sub>O system is plotted in Figure 14, and one can see that lower saturation concentrations for these two points (open squares) would be more consistent with the rest of the data. The comparison between predicted simultaneous solubility of KCl and NaCl in aqueous hydrochloric acid solution is presented in Table 8.

The HCl partial pressure data over H<sup>+</sup>-K<sup>+</sup>-Na<sup>+</sup>-Cl<sup>-</sup> aqueous solutions of ionic strength 5 molal of Clegg & Brimblecombe (1988b, System 5), which was not used to regress any of our model parameters, was used to additionally assess the applicability of our activity coefficient/Henry's law parameterization for the quaternary mixture. Table 9 compares the experimental and predicted values. The average % absolute deviation of the model predictions is 5.64%, reasonable considering the error of the various experimental data used to regress the model parameters. Figure 15 graphically compares our model predictions with the data. The values of the high and low experimental error bars were estimated from Fig. 2b of Clegg & Brimblecombe (1988b). The predictions of our association-based parameterization appear to be similar to those of the authors' own complete-dissociation

parameterization of the Pitzer model (compare our Fig. 15 with Fig. 2b of Clegg & Brimblecombe, 1988b).

### *Temperatures Other Than 25° C*

HCl-NaCl-H<sub>2</sub>O ( $I \leq 17.5$  m; 0-50° C)

The stoichiometric HCl activity coefficients at five-degree increments from 0 to 50° C (excluding data at 25° C) and  $I \leq 3$  m from Harned & Owen (1958) and the solubility of NaCl at 0, 10-10.5, 18, and 30° C and  $6 \leq I \leq 17.5$  m from Linke & Seidell (1965, Vol. II, pg. 962-963), both pertaining to the ternary system, were used to regress the temperature dependency of  $\theta_{H^+,Na^+}$ ,  $\psi_{H^+,Na^+,Cl^-}$ , and  $(\lambda_{(HCl, Cl^-)} + \lambda_{(HCl, Na^+)})$ . Isothermal regressions were performed at the temperatures where both activity coefficient and solubility data were available (0, 10, 18, and 30° C). The temperature of 10° C was assumed for the solubility data at 10-10.5° C, and activity coefficient data at 18° C was obtained by interpolation of data at 15 and 20° C. None of the parameters varied linearly with temperature, but each had a general upward or downward trend. The coefficient for the inverse temperature term of each Pitzer parameter was estimated, and predictions were calculated for all the data, including the activity coefficient data not used in the isothermal regressions. The parameter set reproduced the activity coefficient data very well (average absolute deviation of 0.4%). However, the solubility data at 10-10.5° C (original source cited as Enklaar, 1901) was reproduced badly - an average absolute deviation of 84.4 % - while the solubility at the other temperatures was reproduced well - an average absolute deviation of only 8.4%. We could not improve the fit of the solubility data at 10-10.5° C without dramatically decreasing the fit of the other data (solubility at other temperatures and the activity coefficient at all temperatures). Consequently, we conclude that the solubility data at 10-10.5° C is consistent neither with the solubility data of the other researchers reported by Linke & Seidell (1965, Vol. II, pg. 962-963) at 0, 18, 25, and 30° C nor with the activity coefficient data of Harned & Owen (1958) reported for 0-50° C.

Therefore, the 10-10.5° C solubility data was excluded, and the coefficients of the inverse temperature term for the Pitzer mixing parameters were regressed using all the other data, with the coefficient estimates from the isothermal regressions used as the initial values. The absolute deviation of the activity coefficient data remained low, and the absolute deviation was reduced to 4.9% for the solubility data. Model predictions are compared with the data in Tables 10 & 11. The last row of Table 11 shows that our parameterization is appreciably inconsistent with one solubility point from Schreinemakers (1909-10) at 30° C - the model would appear to predict a higher NaCl saturation concentration. One can also see in Tbl. 11 that the deviation between the model predictions and the data increases with increasing temperature.

KCl-HCl-H<sub>2</sub>O ( $I \leq 17.3$  m; 0-50° C)

The solubility of KCl over the ionic strength range 3.8-17.3 m at 0° C (Linke & Seidell, 1965, pg. 116) and the activity coefficient data of 0.01 m HCl in KCl solutions of ionic strength up to 3.5 at 5° increments from 0 to 50° C (Harned & Owen, 1958) were used to regress the temperature dependency of  $\theta_{H^+,K^+}$ ,  $\psi_{H^+,K^+,Cl^-}$ , and  $(\lambda_{(HCl, Cl^-)} + \lambda_{(HCl, K^+)})$ , applicable to  $I \leq 17.3$  m. The problems encountered and the process used to regress the parameters have been discussed earlier.

Tables 12 & 13 display the results for solubility at 0° C and the multi-temperature activity coefficient, respectively. One can see from Table 12 that the model adequately predicts the solubility up to an ionic strength of 20.8 m. The average % absolute deviation is calculated for each temperature (shaded cells) in Table 13, and one can see the increasing deviation for the activity coefficient with increasing temperature that was noted earlier in this discussion.



Despite the reasonable fit of the predictions with experimental data for the ternary system KCl-HCl-H<sub>2</sub>O, there exists a systematic pattern in the deviation of the solubility predictions. Figure 16 displays the predicted KCl ionic product at saturation at 0° C in the ternary KCl-HCl-H<sub>2</sub>O system. The predicted saturation ionic product somewhat mimics a sine curve overlaying the thermodynamic solubility product. The same variable at 25° C is displayed in Figure 17, and a sine-wave shape may again be evident.

As mentioned earlier, the initial values of  $\theta_{H^+,K^+}$ ,  $\psi_{H^+,K^+,Cl^-}$ , and  $(\lambda_{(HCl, Cl^-)} + \lambda_{(HCl, K^+)})$  at 25° C determined from a simultaneous regression of data from all ternary subsystems and the quaternary system itself pertaining to HCl-KCl-NaCl-H<sub>2</sub>O had to be adjusted to improve the fit for the activity coefficient data of the ternary subsystem KCl-HCl-H<sub>2</sub>O at temperatures other than 25° C. Even though the initial and final (adjusted) values of these three mixing parameters produce almost identical % absolute deviations for the KCl saturation ionic product at 25° C in the ternary system, the respective patterns of the deviation are different. Figure 18 compares the predicted KCl saturation ionic product with the thermodynamic solubility product at 25° C when the initial parameter values are used. In this case, the oscillation in the ionic product is less like a sine-wave relative to Fig. 17, but the oscillation is not centered around the thermodynamic solubility product.

Figs. 16-18 are clear reminders that fitting Pitzer parameters involves just as much art as science. At least three factors can contribute to systematic patterns in residuals: 1) trying to reconcile different types of data (SLE, VLE, activity coefficient, osmotic coefficient, dissociation constant, and solubility products) at different temperatures and from different researchers of unequal precision by using such techniques as unequal weighting or a series of isothermal regressions vs. a single simultaneous multi-temperature regression to determine temperature-dependent coefficients; 2) the unavoidable arbitrariness of the procedural sequence required to implement the computer regressions, such as the order in which parameters are optimized within the nested convergence iteration scheme; and 3) arbitrary decisions made by the engineer in the methodical attempt to arrive at a global optimization - such as reducing the number of regressed coefficients by assuming a simple linear temperature dependency for a Pitzer parameter, or using a piecemeal approach and arriving at parameter values in a sequential manner. The existence of a residual pattern, indicated by Figs. 16 & 17, suggests that either our final Pitzer parameter values for the HCl-KCl-H<sub>2</sub>O ternary system can still be improved or that there are inconsistencies between the HCl activity coefficient and KCl solubility data that our implementation of the association-based Pitzer approach can not completely overcome.

### **Solubility Extrapolations**

The association-based parameterization of the Pitzer model appears to extrapolate and predict solubility at concentrations slightly higher than the regressed data for the two acid ternary subsystems. The solubility of NaCl in aqueous hydrochloric acid with an ionic strength of 19 m at 25° C is predicted very well (Tbl. 7), as is the solubility of KCl in solution of ionic strength 17.6 m at 25° C (Tbl. 6) and up to 20.8 m at 0° C (Tbl. 12). At these low temperatures and high stoichiometric hydrochloric acid concentrations, the HCl activity coefficient vs. concentration curve is very steep (see Fig. 5), and the ability of the chloride-system model to predict salt solubility several molal units higher than the regressed data implies that the regressed HCl Pitzer parameters have captured the thermodynamic properties of the acid well.

Weber (2000) concluded that binary parameters regressed from a binary solution up to the saturation limit may not be applicable to mixed electrolyte solutions when the ionic strength appreciably exceeds the salt's binary saturation limit. Weber regressed new binary parameters for NaCl and KCl at 25° C applicable to ionic strengths of 12 and 9 molal, respectively, using in part solubility data of the salts in aqueous hydrochloric acid solutions. Our experience with the HCl-KCl

ternary aqueous system may support his conclusion - perhaps the binary Pitzer parameters for HCl and/or KCl need to be determined with the ternary system data included in the regressed data set.

However, our experience here does not support a blanket conclusion that binary parameters regressed from only binary solutions up to the saturation limit are not applicable to electrolyte mixtures of appreciably higher ionic strength. To the contrary, binary parameters of NaCl published in the literature and regressed solely from binary solutions up to the saturation limit were found adequate in our work up to ionic strengths of 19 m at 25° C, which is appreciably higher than the ionic strength limit of 12 m determined by Weber (2000) for his adjusted NaCl binary parameters. Our results suggest that perhaps the HCl parameters were in need of adjustment rather than those of NaCl.

### ***Nitric Acid ( $\text{HNO}_3\text{-H}_2\text{O}$ )***

#### **Osmotic And Activity Coefficient Data**

Clegg & Brimblecombe (1990), assuming complete dissociation of the nitric acid in solution, developed a mole-fraction based activity coefficient model and corresponding Henry's law correlation for 0-100 % nitric acid aqueous solutions at -60 to 120° C. They used some freezing point data, but mostly water partial pressures were used to calculate osmotic coefficients, assuming ideality in the vapor phase and using Eqs. [11] & [12]. Except for some emf measurements at low concentrations at 25° C, they calculated solute activity coefficients in two ways: 1) using the calculated osmotic coefficients and the Gibbs-Duhem relationship, and 2) using nitric acid partial pressure data, an assumed Henry's law constant, and Eq. [A7]. They determined the value of the Henry's law constant at 25° C by optimizing the agreement of activity coefficients calculated from osmotic coefficients, from  $\text{HNO}_3$  partial pressures, and from emf measurements at 25° C. The optimized value of the Henry's law constant at 25° C differs by about 1% from the value determined by Tang et al. (1988).

Clegg & Brimblecombe (1990) used heat capacity data to determine the temperature dependence of the Henry's law constant and develop a correlation for the Henry's law constant relative to its value at 298 K. Similarly, partial molal enthalpy and heat capacity data were used to develop temperature dependent correlations for water activity and solute activity coefficient relative to their values at the reference temperature 298 K (Eqs. 18, 19, 29, 30, and Chebychev polynomial coefficients given in Tbls. XII-XV of Clegg & Brimblecombe (1990)). The predictions of the correlation for water activity at temperatures other than 25° C were compared to experimental values calculated from multi-temperature water partial pressure data and Eq. [11]. The correlation for solute activity coefficient was assessed by comparing its predictions to experimental values calculated from multi-temperature nitric acid partial pressure data and their correlation for the Henry's law constant.

Clegg & Brimblecombe (1990) found data inconsistencies and had to judiciously exclude some data points and assign unequal weighting to the different data types. The deviations of their model's predictions from the data normalized to the reference temperature of 298 K is as high as 30% in some cases, and there are no apparent trends of the residual with respect to temperature or concentration (see Figs. 8, 9, & 12 of Clegg & Brimblecombe (1990)).

The inconsistency in the published literature for vapor-liquid equilibrium data of aqueous nitric acid is appreciable, so the task undertaken by Clegg & Brimblecombe (1990) was formidable. The I.C.T. (pg. 309) has VLE data for aqueous nitric acid covering a good range of total pressure and temperature and cites Pascal & Garnier (1923) as the original source. Clegg & Brimblecombe (1990) cite Berl & Samtleben (1922) and Carpenter & Babor (1924/25) on their list of VLE data sources. All three of these original data sources, however, are claimed to be inaccurate by Ellis & Thwaites (1957). Sproesser and Taylor (1921) saw consistency between their own data and that of Burdick & Freed (1921) but disagreement with that of Creighton & Githens (1915), all three of which are on the citation list of the I.C.T. (pp. 304-305) data at saturation pressure.

Figure 19 compares calculated osmotic coefficients at 25° C, using Eqs. [11] & [12], from two sources of water partial pressure data used by Clegg & Brimblecombe (1990) - Davis & De Bruin (1964) and Yakimov & Mishin (1964) - with the recommended values of Hamer & Wu (1972). The functional form of the transformed data of Yakimov & Mishin (1964) is uncharacteristic compared to that of Hamer & Wu (1972), and the transformed value of Davis & De Bruin (1964) of 1.86 at  $m^{0.5}=1.8$  is extremely high. One group of points with relatively little spread is circled, and its error band is approximately  $\pm 3.5\%$ , giving some indication of the minimal experimental uncertainty for osmotic coefficient that could be expected from these two sets of VLE data (Yakimov & Mishin and Davis & De Bruin).

Similarly, Figure 20 compares calculated osmotic coefficients at 20° C from two additional sources of water partial pressure data used by Clegg & Brimblecombe (1990) - Sproesser & Taylor (1921) and Potier (1957). The discrepancy between the two is appreciable.

Figures 21 & 22 compare nitric acid partial pressure data (at saturation pressure) used to calculate stoichiometric nitric acid activity coefficients from Henry's law by Clegg & Brimblecombe (1990) at 25 and 50° C, respectively. At a concentration of 0.8 m at 25° C, there is an order of magnitude difference between the experimental values of Tang et al. (1988) and Burdick & Freed (1921). The fact that the values of the Henry's law constant at 25° C determined by Clegg & Brimblecombe (1990) and Tang et al. (1988) agree to within 1% of each other suggests that Clegg & Brimblecombe (1990) gave more weight to the data of Tang et al. (1988) than to the data of Burdick & Freed (1921). The data of Burdick & Freed (1921) appears to be generally on the high side at 50° C as well. A group of points with relatively little spread is circled in Fig. 22, representing an error band in atmospheres of approximately  $\pm 15\%$ . It appears that data agreement between different researchers decreases with decreasing concentration.

Given the appreciable data inconsistencies, only a few of which we have highlighted in Figs. 19-22, the model of Clegg & Brimblecombe (1990), with its maximum residual of 30% and an apparent lack of systematic residual patterns, is considered to be an outstanding achievement. Even though the model developed by Clegg & Brimblecombe (1990) was mole-fraction based and is not available in the physical properties model library of ASPEN Plus, their multi-temperature correlation for nitric acid stoichiometric activity coefficient referenced to 298 K can be used to estimate multi-temperature activity coefficient values that can then be used as "data" input to fit parameters for any other model of one's choosing, such as the molality-based Pitzer formalism. We chose this route because (a) we are not aware of any activity coefficient data in the published literature for the HNO<sub>3</sub>-H<sub>2</sub>O system at temperatures above 25° C, and (b) we believe the Clegg & Brimblecombe correlation credible because of its relatively good compatibility with a large, multi-temperature VLE data set.

In light of the data difficulties described above, we used the recommended values of Hamer & Wu (1972) and Redlich et al. (1968) to fix the osmotic and activity coefficients from 0-20 molal at the reference temperature of 25° C. The data of Hamer & Wu (1972) was chosen for the reference-temperature standard because it is commonly cited, and that work incorporated several of the data sources used by Clegg & Brimblecombe (1990). The data of Redlich et al. (1968) was included in the reference-temperature standard set because it was transformed from VLE data while remaining in relative agreement with the data of Hamer & Wu (1972). We then used the multi-temperature correlation of Clegg & Brimblecombe (1990) for solute activity coefficient to create "data" input for stoichiometric molal activity coefficients at ten degree intervals from 0 to 110° C. One needs to remember that this created database will not exactly match the predictions of the mole-fraction model of Clegg & Brimblecombe (1990) because they did not use the data of Hamer & Wu (1972) and Redlich et al. (1968) to set the base values of water activity and solute activity coefficient at the reference temperature 298 K.

## Dissociation Data

The spread in experimental dissociation data for  $\text{HNO}_3$  at 25° C can be seen in Figure 24 where the results of five studies are displayed. Davis and De Bruin (1964) discuss the difficulty of experimentally determining a consistent set of activity and fraction of dissociation ( $\alpha$ ) data, and they concluded that uncertainties in the values of activities, dissociation, and  $K_{D, \text{HNO}_3}$  were in the range 10-20%. The authors analyzed several sets of activity and dissociation data to generate a recommended set of consistent data. Among the dissociation data they incorporated into their work were the results of Krawetz (1955), Hood & Reilly (1960), and Axtmann et al. (1960). Fig. 24 shows that the results of Davis and De Bruin (1964), Krawetz (1955), and Hood & Reilly (1960) appear consistent, and therefore, were used in our regression. The data of Axtmann et al. (1960) and Hood et al. (1954), however, appear to be outliers and were, therefore, not used.

Axtmann et al. (1960) also have dissociation data at 40, 60, and 80° C, but it seems inconsistent with the expected trend of monotonic decrease with temperature. For example, below 5 molal dissociation at both 60 and 80° C are greater, rather than less, than that at 40° C. Above 11 molal, however, the data follows the trend of decreasing dissociation with increasing temperature, which is the trend the data of Hood & Reilly (1960) and Krawetz (1955) show at all molalities up to 20 m. The data of Axtmann et al. (1960) at three concentrations at 40, 60, and 80° C is plotted in Figure 24. The uncommon dependence of dissociation on temperature displayed in Fig. 24 and the apparent deviations at 25° C displayed in Fig. 23 caused us to exclude the Axtmann et al. (1960) dissociation data altogether.

Hood & Reilly (1960) provide dissociation data at 0, 25, and 70° C, which we believe is credible because their data at 25° C is consistent with that of several other researchers, they critically evaluated their previous studies and were not afraid to propose improved values, and their data displayed the common trend of decreasing dissociation with increasing temperature. Because of the appreciable experimental uncertainties that can arise with dissociation data at even just one temperature (see Fig. 23), it was considered prudent to use multi-temperature data from one source to avoid the noise that could arise from using data from different researchers at different temperatures. The data of Axtmann et al. (1960) at 80° C, for example, has higher dissociation values than that of Hood & Reilly (1960) at 70° C, but both may be within the experimental uncertainty for that ten-degree interval. Consequently, the dissociation data of Hood & Reilly (1960) was chosen as the multi-temperature data set because of its apparent credibility and its large temperature range (the work of Krawetz (1955) was limited to 50° rather than 70° C).

In summary, in order to fit association-based Pitzer model parameters for aqueous nitric acid up to 20 molal and 0-110° C, we chose to use (a) the multi-temperature dissociation data of Hood & Reilly (1960), (b) the dissociation data of Davis & De Bruin (1964) and Krawetz (1955) at 25° C, (c) the osmotic and activity coefficient data of Hamer & Wu (1972) at 25° C, (d) the activity coefficient data of Redlich et al. (1968) at 25° C, and (e) the multi-temperature activity coefficient databank derived from the Clegg & Brimblecombe referenced-based correlation.

### Concentration Limit of Model

Although the Pitzer model has practical concentration limits due to its molality-based approach, it may be applied with some confidence up to moderately high concentrations (16 molal for HCl and 20 molal for  $\text{HNO}_3$ ) using the parameters developed in this work, based on the data comparisons presented herein.

Data for the  $\text{HNO}_3$ - $\text{H}_2\text{O}$  system, however, exists for concentrations much higher than 20 molal. Redlich et al. (1968) gives osmotic and activity coefficient values up to pure nitric acid at 25° C. Davis & De Bruin (1964) give activity coefficient and dissociation data up to near-pure nitric acid at 25° C. Hood & Reilly (1960) give dissociation data up to 50 molal at 0, 25, and 70° C. The activity coefficient correlation of Clegg & Brimblecombe (1990) based on the reference temperature 298 K

also extend to concentrations much higher than 20 molal. Consequently, a multi-temperature, association-based, Pitzer model could possibly be parameterized that would extend to concentrations much higher than 20 molal. 20 molal, however, was chosen as the threshold concentration for our model because that is the point at which the trend in activity coefficient data from various researchers appear to diverge. This can be seen in Figure 25; values from Davis & De Bruin (1964) and Redlich et al. (1968) were transformed to the molality scale.

The osmotic and activity coefficient data of Redlich et al. (1968) could be used to fix their values at the reference temperature of 25° C, from which one could generate a multi-temperature activity coefficient databank from the temperature-dependent correlation of Clegg & Brimblecombe (1990). This data, coupled with the multi-temperature dissociation data of Hood & Reilly (1960), would permit the assessment of an association-based Pitzer model applicable to concentrations exceeding 20 molal. Such an exercise would provide insights into the true limits of an association-based Pitzer formalism.

One can also see in Fig. 25 the appreciable difference between the activity coefficient values of Hamer & Wu (1972) and those of Davis & De Bruin (1964) at 25° C. Interestingly, Redlich et al. (1968) determined their values mostly from vapor pressure data but agree more with the results of Hamer & Wu (1972) than the vapor-pressure based results of Davis & De Bruin (1964). Also interesting is that both Hamer & Wu (1972) and Redlich et al. (1968) considered the results of Davis & De Bruin (1964) in their studies, and yet both determined a set of recommended activity coefficient values significantly different from those of Davis & De Bruin (1964). Redlich et al. (1968) state that they saw appreciable discrepancies between the vapor pressure data of Davis & De Bruin (1964) and that of their other three sources, one of which was Potier (1957). Clegg & Brimblecombe (1990) cite both Davis & De Bruin (1964) and Potier (1957) as sources of vapor pressure data they used to develop their mole-fraction based model. These facts re-emphasize two points previously made - that much inconsistency exists within the published literature for HNO<sub>3</sub>-H<sub>2</sub>O VLE data, and that our multi-temperature activity coefficient databank generated from the Clegg & Brimblecombe (1990) correlation referenced to 298 K will deviate somewhat from the predictions of the Clegg & Brimblecombe (1990) mole-fraction model.

## Regression of Pitzer Parameters and Equilibrium Constant

In contrast to our treatment of hydrochloric acid, we included the ternary neutral interaction parameter  $\mu_{(\text{HNO}_3, \text{HNO}_3, \text{HNO}_3)}$  in the HNO<sub>3</sub> parameterization because it reduced the discrepancy between data and model predictions by about 27% during preliminary regressions of multi-temperature activity/osmotic coefficient and dissociation data. The temperature-dependent coefficients of the correlations for the dissociation constant and Pitzer parameters (Eqs. [9] & [10], respectively) were regressed in two phases, as described below.

### *Dissociation Constant ( $K_{D,\text{HNO}_3}$ )*

Phase I consisted of determining the temperature dependence of the equilibrium constant. Isothermal regressions of the Pitzer parameters and dissociation constant were performed at the three temperatures for which dissociation data was had - 0, 25, and 70° C. The values of the equilibrium constant at the three temperatures were fit well to the van't Hoff expression ( $R^2 = 0.99899$ ),

$$\ln K_{D,\text{HNO}_3} = -1.56132 + 1325.9097/T, \quad [14]$$

where T is in degrees Kelvin. The values of the equilibrium constant given by Eq. [14] at the three temperatures above are 26.92, 17.92, and 10.00. Literature values at 25° C range from 1.2 (Sillen & Martell, 1964, pgs. 166-167) to 195 (Sampoli et al., 1985), with the majority of researchers reporting values in the 20-25 range (Robinson & Stokes, 1959, pg. 378; Hood et al., 1954; and Marshall & Slusher, 1975). Table 14 compares the values given by Eq. [14] with the estimates of the researchers

whose dissociation data was used in the regressions as well as estimates of other researchers. Eq. [14] is in satisfactory agreement with values from the literature but appears to be on the low side, particularly at 0° C.

### ***Pitzer Parameters***

In Phase II, the equilibrium constant given by Eq. [14] was used to perform isothermal regressions of the Pitzer parameters at 85° C and at ten-degree intervals from 10-60 and 80-110° C. For all Pitzer parameters, the values regressed earlier at 70° C in Phase I were inconsistent with the values from these new isothermal regressions. This suggests that the dissociation data of Hood & Reilly (1960) may be inconsistent with the activity coefficient values calculated from the Clegg & Brimblecombe (1990) correlation (which uses our set of activity and osmotic coefficient values at the reference temperature 25° C). It is interesting that this inconsistency appears at 70° C, where the regressed value of the equilibrium constant is relatively consistent with other literature values, rather than at 0° C, where the regressed value of the equilibrium constant is about 39% lower than the literature (see Tbl. 14). One would expect such an inconsistency to be more probable at the temperature of the largest discrepancy of the equilibrium constant rather than at the temperature of the highest agreement of the equilibrium constant.

Because the outlying nature of the 70° C values of the Pitzer parameters, the coefficients of Eq. [10] were fitted for each Pitzer parameter excluding the values at 70° C. As representative plots, Figures 26 & 27 display the isothermal regressed values for  $\beta_{(H^+, NO_3^-)}^0$  and  $\psi_{(HNO_3, HNO_3, HNO_3)}$ , respectively, together with their fitted curves using Eq. [10]. ASPEN Plus uses the  $\Psi$  (psi) parameter for the ternary interaction between three neutral species as well as ions, and when used as such it is equivalent to the Pitzer ternary interaction parameter  $\mu$  (mu) multiplied by six (Aspen Technology, 2001). The  $\psi_{(HNO_3, HNO_3, HNO_3)}$  parameter displayed in Fig. 27 is thus equal to  $6 * \mu_{(HNO_3, HNO_3, HNO_3)}$ . The inconsistency of the 70° C (343 K) values is apparent.

### ***Results***

Extent of dissociation, osmotic coefficient, and activity coefficient values for 0-20 molal and 0-110° C were predicted using the equilibrium constant correlation from Phase I and the Pitzer parameter correlations determined from Phase II. The predictions vs. regressed data for dissociation are displayed in Figure 28 and tabulated in Table 15. The average absolute percent deviation is 0.94, 1.01, and 4.58 for 0, 25, and 70° C, respectively (shaded cells in Tbl. 15). As expected, the deviation at 70° C is the highest, but acceptable given the scatter and potential error in experimental dissociation data (see Figs. 23-22). Model predictions are compared with the unregressed data of Krawetz (1955) at 0 and 50° C in Figure 29. The regressed data of Hood & Reilly (1960) at 0° C are displayed as a reference in Fig. 29, and the difference between it and that of Krawetz (1955) provides another example of the data variation among researchers. The predictions of our parameterization of the Pitzer model have an average absolute deviation of 3.61% at 0 and 3.39% at 50, relative to the unregressed data of Krawetz (1955). The predicted extents of dissociation at ten-degree increments within the regressed temperature range of 0-110° C and extrapolations to 125, 150, and 175° C are graphed in Figure 30.

The average absolute deviation from the experimental activity coefficient data of Hamer & Wu (1972) and Redlich et al. (1968) at 25° C is 0.51%, and is tabulated in Table 16. The average absolute deviation from the “data” of the Clegg & Brimblecombe (1990) activity coefficient correlation is 0.14%. The global absolute deviation for the entire temperature range 0-110° C is 0.17%. The data and model predictions within and outside the regressed temperature range are displayed in Figure 31. The average absolute deviation from the experimental osmotic coefficient data

of Hamer & Wu (1972) at 25° C is 0.32%. Model predictions are compared with data at 25° C in Figure 32 and Table 16. Multi-temperature predictions are displayed in Figure 33.

The values of the activity coefficient of the associated nitric acid molecule at 25° C predicted by the model and those calculated from the stoichiometric molal activity coefficients, extents of dissociation, and equilibrium constant (=18.8) of Davis & De Bruin (1964) are of the same order of magnitude, as can be seen in Figure 34. Multi-temperature predictions of the model are displayed in Figure 35. The curve of the activity coefficient vs. stoichiometric concentration changes form between 90 and 100° C. From 0-90° C, the curve monotonically increases from a value of one at infinitely dilute. At 100° C and above, however, the curve is a parabola, with a minima lower than one. Note that the temperature dependency displayed in Fig. 35 for nitric acid is the reverse of that displayed for HCl in Fig. 10 - at a given concentration, the activity coefficient decreases with increasing temperature in the case of molecular nitric acid but increases with increasing temperature for molecular HCl.

Dissociation and activity coefficient data were given equal weight in the regressions because both data types appear to have comparable error bands (see Figs. 23-25). Therefore, since data quality doesn't appear to favor an unequal weighting scheme, we chose to keep the current equilibrium and Pitzer parameter correlations as regressed, despite the relatively poorer fit to the dissociation data at 70° C. However, weighting schemes are subjective, and one could give more weight to the dissociation data with the intent to improve the fit with the extent of dissociation at 70° C, for example, at a probable cost of less fit with the activity coefficient values from the Clegg & Brimblecombe (1990) correlation.

### Henry's Law Constant and Vapor-Liquid Equilibrium

Because of the lack of agreement between various published VLE data for the HNO<sub>3</sub>-H<sub>2</sub>O system, which has been discussed earlier (see Figs. 19-22), it is not possible to arrive at an activity coefficient and Henry's law model that fit all the VLE data. We tried two approaches. In the first, we used Eq. [A9] and our correlation for the dissociation constant (Eq. [10]), to transform an association-based correlation for the Henry's law constant in ASPEN Plus' functional form (Eq. [9]) from the complete-dissociation Henry's law correlation of Clegg & Brimblecombe (1990, Eqs. 5 & 40).

In the second approach, we used the temperature correlations previously regressed for the equilibrium constant and Pitzer parameters and performed isothermal regressions of the Henry's law constant at 5-120° C using the VLE data of Perry & Green (1997). The temperature-dependent correlation for the Henry's law constant was then fitted from the isothermal results. Perry & Green (1997) was chosen for several reasons: 1) it is a common reference for chemical process engineers, the main targeted users of the model; 2) it provides a single (and hopefully reasonably consistent) set of data at five-degree increments from 5 to 125° C; and 3) it appears to be the same as the I.C.T. (pp. 304-305) data at saturation pressure, and thus, it incorporates some VLE data used by Clegg & Brimblecombe (1990) as well as some unique data.

One would not expect appreciably different Henry's law constant values because our Pitzer activity coefficient model was parameterized from the temperature-dependent correlation of Clegg & Brimblecombe (1990), but one would expect some difference because of the differences between the data of Perry & Green (1997) and that used by Clegg & Brimblecombe (1990). Also, one would expect that the second approach would result in a better fit to the Perry & Green (1997) data since that data was used to regress the Henry's law constant. Figures 36 and 37 show that such is the case.

The resulting Henry's law constants from both approaches are plotted in Fig. 36. The two curves overlay up to room temperature and then diverge. The Perry & Green (1997) data is compared with the predictions of both approaches in Fig. 37. The predictions of the two approaches were essentially the same at 0 and 25° C, consistent with Fig. 36. At higher temperatures, the predictions of

the transformed Clegg & Brimblecombe (1990) Henry's law constant (transformed CB) are lower than those of the regressed Henry's law constant. It appears that the transformed Henry's law constant fits the data better around  $m > 16$  for  $T \geq 50^\circ \text{C}$ . This difference is logical given the fact that the transformed CB constant was developed from data with concentrations up to 100% nitric acid and its value at the reference temperature of  $25^\circ \text{C}$  has a strong preference for the  $\text{HNO}_3$  partial pressure data of Tang et al. (which has lower values than some other data sources; see Fig. 21). Overall, the regressed Henry's law constant has an average absolute deviation of 14.0% to the Perry & Green (1997) data, compared to 19.3% for the transformed CB.

A comparison of the two approaches with the high-temperature VLE data of Ellis & Thwaites (1957), which was not used in the regressions of approach #2 nor cited by Clegg & Brimblecombe (1990), is shown in Table 17. The trends evident with the data of Perry & Green (1997) also appear with that of Ellis & Thwaites (1957) - the regressed Henry's law constant is somewhat better at all but the high-molality data point (20.12 m). Both Henry's law constants are included in Table 20. Given the large disagreement among the vapor-liquid equilibrium data for aqueous nitric acid, however, we do not feel that either of the Henry's law constant correlations can claim predictive superiority.

It is clear that despite being a much-studied system, the thermodynamics of aqueous nitric acid are not as well understood as for other systems. Figs. 23-25 support the conclusion of Davis & De Bruin (1964) that there is appreciable uncertainty in experimental values of activity coefficients, extents of dissociation, and dissociation constants. Figs. 19-22 show the large disagreement in VLE data for the system and help explain why Clegg & Brimblecombe (1990) had deviations up to 30% with their mole-fraction model.

Our association-based parameterization for the  $\text{HNO}_3\text{-H}_2\text{O}$  system appears to be within experimental error and is unique in that as a molality-based Pitzer model it predicts chemical equilibrium as well as vapor-liquid equilibrium and the usual properties of activity and osmotic coefficients.



## COMPARISON WITH COMPLETE-DISSOCIATION APPROACH

To compare the traditional complete-dissociation and the association-based approaches, predictions from the two approaches are compared with data for the two acid binary solutions at 25° C. The association-based parameterizations used in this comparison correspond to our final multi-temperature correlations given in Tbls. 18-20. Two complete-dissociation, single-temperature parameterizations are used: (1) obtained by regressing activity and osmotic coefficient data for 0-16 and 0-20 molal for HCl and HNO<sub>3</sub>, respectively, and (2) that given by Pitzer (1991, pg. 100). Equal weighting for the two data types - stoichiometric molal activity coefficient and osmotic coefficient - and for all concentrations was used in the extended complete-dissociation parameterization we present here as was done for our association-based parameterization. The complete-dissociation parameterizations of Pitzer (1991) are only used to compare results for  $m \leq 6$  because that was their targeted concentration range. The comparison results are summarized in Table 21.

### *Comparison With Traditional, Low-Molality, Complete-Dissociation Model*

#### Hydrochloric Acid

$$m \leq 6$$

The average absolute deviation of the predicted stoichiometric molal activity coefficient of aqueous HCl calculated with the complete-dissociation binary parameters given by Pitzer (1991) for all the regressed activity coefficient data used in our work in the 0-6 molal range is 0.39%, compared to 0.30% for our association-based parameterization. When the data is limited to just that of Robinson & Stokes (1959) for 0-6 molal, data that is commonly cited, the predictions using the complete-dissociation parameterization given by Pitzer (1991) have an average absolute deviation of 0.43%, compared to 0.31% for our association-based.

#### *Performance of Association-Based Model Over Larger Concentration Range ( $m \leq 16$ )*

The average absolute deviation of the predicted stoichiometric molal activity coefficient of aqueous HCl from all the regressed data for 0-16 molal is 0.43% for our association-based approach, which is close to the 0.39% deviation of the Pitzer (1991) parameterization for the limited molality range 0-6 molal. The results were similar for osmotic coefficient, where the average absolute deviation for the association-based parameterization for 0-16 molal (0.19%) is close to that of the Pitzer (1991) complete-dissociation parameterization limited to 6 molal (0.17%). Consequently, accounting for association in a strong acid allows the Pitzer model to predict up to high molalities with the same accuracy of the traditional Pitzer model at low molalities - 0.41 vs. 0.39% for activity coefficient and 0.19 vs. 0.17% for osmotic coefficient in the case of HCl.

#### Nitric Acid

$$m \leq 6$$

The average absolute deviation of the predicted stoichiometric molal activity coefficient of aqueous HNO<sub>3</sub> calculated with the complete-dissociation binary parameters given by Pitzer (1991) for all the regressed activity coefficient data used in our work in the 0-6 molal range is 0.36%, compared to 0.54% for our association-based parameterization. When the data is limited to just that of Hamer & Wu (1972) for 0-6 molal, from which the parameters in Pitzer (1991) were regressed, the predictions using the complete-dissociation parameterization given by Pitzer (1991) have an average absolute deviation of 0.19%, compared to 0.43% for our association-based.

### ***Performance of Association-Based Model Over Larger Concentration Range ( $m \leq 20$ )***

The average absolute deviation of the predicted stoichiometric molal activity coefficient of aqueous  $\text{HNO}_3$  from all the regressed data for 0-20 molal is 0.44% for our association-based approach, which is appreciably larger than the 0.19% deviation of the Pitzer (1991) parameterization for the limited molality range 0-6 molal. The results were similar for osmotic coefficient, where the average absolute deviation for the association-based parameterization for 0-20 molal (0.32%) is appreciably larger than that of the Pitzer (1991) complete-dissociation parameterization limited to 6 molal (0.09%).

Unlike HCl, the association-based parameterization for  $\text{HNO}_3$  up to 20 molal has worse predictive accuracy than that of the complete-dissociation approach limited to 6 molal, about double the average absolute deviation for activity coefficient (0.44 vs. 0.19%) and about 3.5 times greater (0.32 vs. 0.09%) for osmotic coefficient. There were three constraints, other than the increased concentration range, imposed upon the association-based parameterization that were not imposed upon the complete-dissociation parameterization of Pitzer (1991) that may explain the larger deviation of the association-based parameterization: (1) it is multi-temperature, so the parameter values at 25° C are constrained by having to merge smoothing with values over the entire 0-120° C range from which they were fitted; (2) the regressed activity coefficient data at 25° C was not limited to just Hamer & Wu (1972); and (3) the objective function included minimizing the deviation from experimental extent of dissociation data.

In order to assess the impact of these three factors, an isothermal regression at 25° C and 0-20 molal was performed for the association-based parameterization with the activity coefficient data restricted to only that of Hamer & Wu (1972). This eliminated the first two factors and allowed us to assess the combined impact of the larger concentration range and the additional constraint of having to minimize extent of dissociation data. Each data type - activity and osmotic coefficient, and extent of dissociation - was given equal weight in this regression, and the Pitzer parameters and dissociation constant were the manipulated variables.

The average absolute deviation of the activity coefficient for 0-20 molal was reduced from 0.44 to 0.34%, still higher than the 0.19% corresponding to the complete-dissociation parameterization limited to 6 molal. There was less improvement with the osmotic coefficient, the average absolute deviation being reduced from 0.32 to 0.26% but still greater than the 0.09% result for the complete-dissociation parameterization. We conclude that the remaining difference in the deviation is due to the additional constraint of having to minimize extent of dissociation data because the differences in the case of HCl, which didn't have the dissociation constraint, were minimal. Consequently, when the solute undergoes significant association (such as  $\text{HNO}_3$ ), the predictive accuracy of the association-based approach for activity and osmotic coefficient can't match that of the traditional Pitzer model at low molalities if the additional capability of predicting extent of dissociation is required.

### ***Comparison With Extended Complete-Dissociation Model***

The extended complete-dissociation parameterization applicable up to 16-20 molal had the highest average deviations in the comparison, 1.51% for activity coefficient and 0.69% for osmotic coefficient in the case of HCl and 1.15% for activity coefficient and 0.74% for osmotic coefficient in the case of  $\text{HNO}_3$ . Besides having relatively larger average deviations, the extended complete-dissociation approach also results in a more pronounced cyclical under predict/over predict pattern, with individual deviations being significantly larger than the average at higher concentrations.

This cyclical pattern of the extended complete-dissociation parameterizations is visible in Figures 38 & 39 where the predictions of the multi-temperature association-based and single-temperature extended complete-dissociation parameterizations, for 0-16 molal in the case of HCl and

0-20 molal in the case of  $\text{HNO}_3$ , are compared with the regressed data, respectively. The extended complete-dissociation parameterization under predicts the activity coefficient of  $\text{HCl}$  by 5.05% at 10.1 molal and over predicts it by 2.68% at 16 molal. The extended parameterization under predicts the activity coefficient of  $\text{HNO}_3$  by 2.0% at 4.5 molal, over predicts it by 2.2% at 14 molal, and then under predicts again at 20 molal by 3.6%.

The amplitude of the cyclical pattern is quantitatively presented in plots of deviation vs. concentration, which are given in Figures 40 & 41 for  $\text{HCl}$  and  $\text{HNO}_3$ , respectively. The deviation pattern of the association-based parameterization for  $\text{HCl}$  shown in Fig. 40 is more random and within a smaller band around zero than is that of the extended complete-dissociation parameterization. Even though a cyclical deviation pattern is not visible for the association-based parameterization of  $\text{HNO}_3$  from the activity coefficient vs. concentration plot (Fig. 39) because of its small amplitude, its cyclical behavior is discernible in the deviation plot of Fig. 41.

It appears from Fig. 41 that the amplitude (% absolute deviation) decreases with increasing concentration for the multi-temperature association-based parameterization of  $\text{HNO}_3$  at 25° C. The average absolute deviation for the association-based parameterization at 6-20 molal is 0.44%, with the largest deviation being 1.3% at 7 molal. The single-temperature extended complete-dissociation parameterization for the same concentration interval, on the other hand, has an average absolute deviation of 1.43%, with the highest value of 3.6% occurring at 20 molal. The superiority of the association-based over the complete-dissociation approach for  $\text{HNO}_3$  at concentrations above 6 molal is evident.

Interestingly, our computation of the complete-dissociation parameterization of Pitzer (1991) limited to 6 molal  $\text{HNO}_3$  produces a cyclical deviation pattern and a negative bias relative to the data of Hamer & Wu (1972). These are visible in Figure 42. Although the  $\text{HNO}_3$  deviation amplitude in the association-based parameterization ( $\approx 1.25\%$  before decreasing) is larger than that of the limited-molality Pitzer (1991) model ( $\approx 0.2\%$ ), its cyclical pattern is appreciably suppressed relative to that of the extended complete-dissociation model (amplitude  $\approx 2.75\%$ ). The improvement of the association-based approach over that of the complete-dissociation approach for  $\text{HNO}_3$  at high concentrations suggests that the association-based approach could be successful in extending the utility of the Pitzer model to concentrations much higher than 6 molal for other associating solutes.  $\text{KNO}_3$  and  $\text{NaNO}_3$ , for example, both of which have dissociation constants smaller than nitric acid, are of particular interest to the thermodynamic modeling of SBW.

## SUMMARY & CONCLUSIONS

The Pitzer model parameterizations proposed here are recommended for 0-110° C at atmospheric pressure for 0-16 molal and 0-20 molal for the chloride system and aqueous HNO<sub>3</sub>, respectively, and are readily usable in ASPEN Plus. An association-based Pitzer activity coefficient model is combined with Henry's law to predict activity/osmotic coefficients and VLE. The chloride model also predicts KCl and NaCl solubility, while the nitric acid model has the unique capability to also predict the extent of dissociation with an average absolute deviation of 1.43%.

The traditional complete-dissociation Pitzer model - limited to the third virial coefficient and using the originally proposed values of  $b$  and  $\alpha_l$  - is known to be very accurate up to 6 molal. We conclude that the association-based approach extends the utility of the molality-based Pitzer model up to 16-20 molal to predict activity/osmotic coefficients. The average absolute deviation of the association-based approach for HCl up to 16 molal, for example, is almost as small as that of the complete-dissociation approach when limited to only 6 molal. In the case of HNO<sub>3</sub>, a solute undergoing significant association, the association-based approach can reproduce activity and osmotic coefficient data reasonably well (average absolute deviation  $\approx 0.4\%$ ) up to 20 molal, as well as accurately predict extent of dissociation. The association-based approach has the additional benefit of allowing the Pitzer model to be fully utilized in commercial simulators, such as ASPEN Plus, that require accounting for association to implement Henry's law. The complete-dissociation approach of the molality-based Pitzer model, on the other hand, produces a significant under predict/over predict cycle in the predicted activity/osmotic coefficients of HCl and HNO<sub>3</sub> when the regressed data extends much past 6 molal. Additionally, the complete-dissociation approach is not fully compatible with some commercial simulators, such as ASPEN Plus.

The parameterization of the model for the H<sup>+</sup>-K<sup>+</sup>-Na<sup>+</sup>-Cl<sup>-</sup> system was achieved by: (a) performing isothermal regressions of HCl-H<sub>2</sub>O activity/osmotic coefficient data to establish temperature-dependent correlations for the HCl binary Pitzer parameters, (b) regressing HCl partial pressure data to establish a temperature-dependent correlation for the Henry's law constant, (c) regressing solubility and activity coefficient data from HCl-KCl and HCl-NaCl ternary subsystems to determine the corresponding Pitzer mixing parameters, and (d) utilizing mixing parameters for KCl-NaCl from the literature. A reasonable dissociation constant for HCl from the literature was used. Although the HCl parameterization predicts extent of dissociation consistent with the rest of the regressed data, the dissociation predictions are not based upon direct data, and as such, can not be validated. Temperature-dependent correlations for the solubility product of KCl and NaCl were obtained from solubility and saturation activity coefficient data reported in the literature.

The parameterization of the model for nitric acid was developed by estimating activity coefficient values at temperatures other than 25° C with the correlation of Clegg & Brimblecombe (1990) as referenced to the values of Hamer & Wu (1972) and Redlich et al. (1968) at 25° C. Isothermal regressions of activity coefficient and extent of dissociation data were then performed at 0, 25, and 70° C. The van't Hoff expression was used to describe the temperature dependence of the dissociation constant from these three isothermal regressions. The resulting temperature-dependent correlation for the dissociation constant is in reasonable agreement with literature sources. Holding the expression for the dissociation constant fixed, isothermal regressions were performed at other temperatures, from which temperature-dependent correlations were fitted for the Pitzer parameters. Dissociation data was used in the parameterization of the nitric acid model; consequently, predicted extents of HNO<sub>3</sub> dissociation are proposed as reasonable representations of reality.

Two Henry's law correlations were obtained by regressing multi-temperature HNO<sub>3</sub> partial pressure data and by transforming the Henry's law constant of Clegg & Brimblecombe (1990) based on complete dissociation. Given the large variation among the vapor-liquid equilibrium data for aqueous nitric acid, however, neither Henry's law constant correlation can claim superiority based upon predictive accuracy.

We are not aware of any other molality-based Pitzer model for aqueous HCl and HNO<sub>3</sub> in the literature that are applicable to such broad concentration and temperature ranges and yet compatible with ASPEN Plus (limited to the third virial coefficient and having values of  $b$  and  $\alpha_i$  as originally proposed by Pitzer). The comparison between predicted and experimental data is summarized in Table 22. The results indicate that predictions deviate more for phase equilibrium than for activity and osmotic coefficients. Given the experimental uncertainties of the data regressed, the average % absolute deviations listed in Tbl. 22 are acceptable to the practicing process simulation engineer. The models presented here can be easily used in ASPEN Plus and provide the practitioner with a superior alternative to ENRTL.

The “SLE” (solid-liquid equilibrium) column of Table 22 shows that the chloride model appears to have the capability to extrapolate and predict solubility at higher concentrations for the two acid ternary subsystems. The solubility of NaCl in aqueous hydrochloric acid with an ionic strength of 19 m at 25° C (Tbl. 7) and the solubility of KCl in solution of ionic strength 17.6 m at 25° C (Tbl. 6) and up to 20.8 m at 0° C (Tbl. 12) are predicted well. The ability of the chloride-system model to predict salt solubility several molal units higher than the ionic strength of the regressed HCl binary data suggests that the regressed HCl Pitzer parameters have captured the thermodynamic properties of the acid well. The comparison between model predictions and individual data sources for the chloride and nitric acid parameterizations are presented in Tables 23 & 24 for regressed and nonregressed data, respectively.

The equilibrium constants (Eq. [9]) and Pitzer parameters (Eq. [10]) regressed in this work are displayed in Tables 19 and 20. Indication is given for those cases where the regressed data (this work) or stated applicability (cited reference) are for a different temperature or concentration range. Using the mixing parameters for the chloride system at temperatures above 50° C involves extrapolation rather than interpolation, but associated problems were mitigated by using linear temperature relationships.

The bulk of the work of parameterization involved the reconciliation of different data types from different researchers, at similar and different temperatures. The objective was to optimize the overall predictive capability of the parameterizations, and so not all the data is reproduced equally well in terms of precision or randomness of deviation. We feel that the main source of this predictive inequality is the presence of data inconsistencies, apparently due to experimental uncertainties. We realize, however, that imperfections in our parameterization methodology could also introduce error. The most notable discrepancies between predictions and data are:

- 1) the parameterization of the HCl-H<sub>2</sub>O model under predicts the partial pressure of hydrochloric acid at temperatures above 50° C and stoichiometric concentrations below 6 molal, relative to the data of Perry & Green (1997; which appears to be the same as I.C.T.) and Sako et al. (1984);
- 2) the parameterization of the HCl-H<sub>2</sub>O model over predicts the value of the stoichiometric HCl molal activity coefficient at  $T \geq 40^\circ \text{C}$  and stoichiometric concentrations greater than 7 molal, relative to the data of Cerquetti et al. (1968). The deviations increase with increasing temperature, reaching  $\approx 12\%$  at 80 C and 11.1 molal;
- 3) attempts to reconcile activity coefficient and solubility data for the HCl-KCl-H<sub>2</sub>O system did eliminate a bias in the previous solubility deviations (Fig. 18) and did appreciably reduce the overall deviation from the data. However, the final parameterization also introduced nonrandomness into the solubility deviations in the form of a sine-wave pattern (Figs. 16 & 17). Additionally, two different sources of HCl activity coefficient data for the ternary system have opposing trends of deviation vs. temperature;

- 4) the parameterization of the chloride model under predicts the value of the stoichiometric HCl molal activity coefficient in the presence of NaCl, relative to the data of Jiang (1996a-b);
- 5) the average absolute deviation in the predicted solubility of NaCl in aqueous hydrochloric acid increases with increasing temperature with respect to the regressed data of Linke & Seidell (1965) in the range 0-30° C. The solubility data at 10-10.5° C had an average absolute deviation of 84% and was, therefore, not used in the regression;
- 6) the regressed temperature-dependent correlation for the dissociation constant of nitric acid appears to predict values on the low end of the ranges published in the literature;
- 7) and the parameterization of the HNO<sub>3</sub>-H<sub>2</sub>O system under predicts the extent of dissociation of nitric acid at 70° C at stoichiometric concentrations below 20.7 molal, relative to the data of Hood & Reilly (1960).

The parameterization of the models presented in this work was largely dependent upon the work of other modelers. The temperature dependency of the hydrochloric acid model utilized predictions of the 0-7 molal traditional Pitzer model parameterization of Holmes et al. (1987) to provide estimates for activity/osmotic coefficients at 90-110° C. The temperature dependence of the nitric acid model relied on the work of Clegg & Brimblecombe (1990) to give activity coefficient estimates above and below room temperature. These researchers used enthalpy, density, and heat capacity data to model the temperature dependence of the activity coefficient. Their work supplied important missing “data.” In the case of HNO<sub>3</sub>, the data gap was extensive, and the supplied missing data was essential.

Lastly, for those whose modeling conditions and/or software environment are amendable to ignoring association, the low-temperature Henry’s law correlation from Carslaw et al. (1995) was combined with our higher-temperature correlation to generate the complete-dissociation Henry’s law constant (defined by Eq. [A7]) applicable for -90 to 110° C:

$$\ln(H_{HCl}^d) = 357.4334 - \frac{3129.6252}{T} - 62.0944 * \ln(T) + 0.071717 * T. \quad [13]$$

## PATH FORWARD

It is recommended that near-term efforts of Pitzer parameter regression using an association-based approach be focused on the following:

- Elimination of the systematic pattern in the solubility and activity coefficient deviations for the HCl-KCl-H<sub>2</sub>O system.
- Regression of parameters for the H<sup>+</sup>-K<sup>+</sup>-Na<sup>+</sup>-NO<sub>3</sub><sup>-</sup> system because nitrate is the most abundant anion in SBW. The nitric acid binary parameters determined in this work will be utilized.
- Parameterization of an association-based Pitzer model capable of predicting the chemical and phase equilibria of mercury-based complexes of chloride and nitrate. The developed chloride and nitrate models will be utilized
- Regression of mixing parameters for the HCl-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-HF-H<sub>2</sub>O system to support ASPEN modeling of treatment processes for SBW. This is necessary due to the high acidity of SBW. Ternary data of multi-acid systems from the literature will be utilized.
- Regression of interaction parameters for aluminum due to its high concentration in SBW and its tendency to complex in solution.

In the long term, it is also recommended that the following activities be included in order to model complex electrolyte solutions that exist throughout the DOE complex.

- Testing the concentration limit of the association-based approach by extending the HNO<sub>3</sub> parameterization past 20 molal (multi-temperature dissociation data for nitric acid exists up to 50 molal). This will help determine if the semi-empirical nature of the Pitzer approach enables the Pitzer model to be used for higher-concentration SBW treatment processes, such as direct evaporation.
- Assessing the ability of the Pitzer approach to model hydrocarbon molecular solutes in INEEL's complex electrolyte mixtures.

The above activities have scientific merit, applicability to the treatment of liquid SBW at INEEL, and applicability to the treatment of other DOE wastes complex wide.

## REFERENCES

- Akerlof, Gosta and John W. Teare, (1937), "Thermodynamics Of Concentrated Aqueous Solutions Of Hydrochloric Acid", *Journal of the American Chemical Society*, Vol. 59, October, pp. 1855-1868.
- Aspen Technology (2001), *Aspen Physical Property System: Physical Property Methods and Models 11.1*, Ch. 1 "Overview of Aspen Physical Property Methods"(pg. 1-11), Ch. 3 "Property Model Descriptions" (pgs. 3-72 & 3-110), and Appendix C: Pitzer Activity Coefficient Model, September, Aspen Technology, Inc.: Cambridge, MA.
- Axtmann, Robert C., Woodfin E. Shuler, and Bruce B. Murray (1960), "Proton Resonance Shifts In Nitric Acid Solutions Of Aluminum Nitrate", *Journal of Physical Chemistry*, Vol. 64, No. 1, January, pp. 57-61.
- Berl, E. and O. Samtleben (1922), *Z. Angew. Chem.*, Vol. 35, 201.
- Burdick, Charles L. and E. Stanley Freed (1921), "The Equilibrium Between Nitric Oxide, Nitrogen Peroxide And Aqueous Solution Of Nitric Acid", *Journal of the American Chemical Society*, Vol. 43, pp. 518-530.
- Carpenter, C.D. and J.A. Babor (1924/25), *Trans. Amer. Inst. Chem. Engr.*, Vol. 16, 111. Both Ellis & Thwaites (1957) and Clegg & Brimblecombe (1990) cite this source with the same volume and page numbers, but a different year, 1924 and 1925, respectively.
- Carslaw, Kenneth S., Simon L. Clegg, and Peter Brimblecombe (1995), "A Thermodynamic Model of the System HCl-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O, Including Solubilities of HBr, from <200 to 328K", *Journal of Physical Chemistry*, Vol. 99, No. 29, pp. 11557-11574.
- Chen, Chau-Chyun, H.I. Britt, J.F. Boston, and L.B. Evans (1982), "Local Composition Model for Excess Gibbs Energy of Electrolyte Systems, Part I: Single Solvent, Single Completely Dissociated Electrolyte Systems", *AIChE Journal*, Vol. 28, No. 4, July, 1982, pp. 588-596.
- Christov, Christomir (2001), "Thermodynamic Study Of The K-Mg-Al-Cl-SO<sub>4</sub>-H<sub>2</sub>O System At The Temperature 298.15 K", *Calphad*, Vol. 25, No. 3, pp. 445-454.
- Clegg, Simon L. and Peter Brimblecombe (1988a), "Equilibrium Partial Pressures Of Strong Acids Over Concentrated Saline Solutions - I. HNO<sub>3</sub>", *Atmospheric Environment*, Vol. 22, No. 1, pp. 91-100.
- Clegg, Simon L. and Peter Brimblecombe (1988b), "Equilibrium Partial Pressures Of Strong Acids Over Concentrated Saline Solutions - II. HCl", *Atmospheric Environment*, Vol. 22, No. 1, pp. 117-129.
- Clegg, Simon L. and Peter Brimblecombe (1990), "Equilibrium Partial Pressures and Mean Activity and Osmotic Coefficients of 0-100% Nitric Acid as a Function of Temperature", *Journal of Physical Chemistry*, Vol. 94, No. 13, pp. 5369-5380.
- Conceicao, M., P. de Lima, and Kenneth S. Pitzer (1983), "Thermodynamics Of Saturated Aqueous Solutions Including Mixtures Of NaCl, KCl, and CsCl", *Journal of Solution Chemistry*, Vol. 12, No. 3, pp. 171-185.
- Creighton and Githens (1915), *J. Franklin Inst.*, Vol. 179, 161.
- Davis, W., Jr. and H.J. De Bruin (1964), "New Activity Coefficients Of 0-100 Per Cent Aqueous Nitric Acid", *Journal of Inorganic Nuclear Chemistry*, Vol. 26, pp. 1069-1083.
- Denbigh, Kenneth (1981), *The Principles of Chemical Equilibrium*, 4<sup>th</sup> Edition, Cambridge University Press: New York.
- Dinane, Abderrahim, Mohamed El Guendouzi, and Abdelfetah Mounir (2002), "Hygrometric Determination Of Water Activities, Osmotic And Activity Coefficients Of (NaCl + KCl)<sub>(aq)</sub> At T = 298.15 K", *Journal of Chemical Thermodynamics*, Vol. 34, Iss. 4, April 1, pp. 423-441.
- Ellis, S.R.M. and J.M. Thwaites (1957), "Vapour-Liquid Equilibria Of Nitric Acid-Water-Sulphuric Acid Mixtures", *Journal of Applied Chemistry*, Vol. 7, April, pp. 152-160.
- Enklaar, J.E. (1901), *Rec. Trav. Chim.*, Vol. 20, 183.
- Felmy, Andrew R., and Dhanpat Rai (1999), "Application of Pitzer's Equations for Modeling the Aqueous Thermodynamics of Actinide Species in Natural Waters: A Review", *Journal of Solution Chemistry*, Vol. 28, No. 5, May, pp. 533-553.
- Felmy, Andrew R., Lisa M. Onishi, Nancy S. Foster, James R. Rustad, Dhanpat Rai, and Marvin J.



- Mason (2000), "An Aqueous Thermodynamic Model For The  $\text{Pb}^{+2}$  - $\text{Na}^{+}$  - $\text{K}^{+}$  - $\text{Ca}^{+2}$  - $\text{Mg}^{+2}$  - $\text{H}^{+}$  - $\text{Cl}^{-}$  -  $\text{SO}_4^{-2}$  - $\text{H}_2\text{O}$  System To High Concentration: Application To WIPP Brines", *Geochim. Cosmochim. Acta*, Vol. 64, No. 21, pp. 3615-3628.
- Fritz, J.J. and C.R. Fuget (1956), "Vapor Pressure of Aqueous Hydrogen Chloride Solutions, 0° to 50° C", *Industrial and Engineering Chemistry*, Vol. 1, No. 1, pp. 10-12.
- Greenberg, Jerry P. and Nancy Moller (1989), "The Prediction Of Mineral Solubilities In Natural Waters: A Chemical Equilibrium Model For The Na-K-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O System To High Concentration From 0 To 250° C", *Geochimica et Cosmochimica Acta*, Vol. 53, pp. 2503-2518.
- Hamer, Walter J., and Yung-Chi Wu (1972) "Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25° C", *Journal of Physical and Chemical Reference Data*, Vol. 1, No. 4, pp. 1047-1099.
- Harned, Herbert S. and Benton B. Owen (1958), *The Physical Chemistry Of Electrolytic Solutions*, 3rd Edition, Reinhold Publishing Corporation: New York.
- Hawkins, J. Erskine (1932) "The Activity Coefficients Of Hydrochloric Acid In Uni-Univalent Chloride Solutions At Constant Total Molality", *Journal of the American Chemical Society*, Vol. 54, December, pp. 4480-4487.
- Hellams, K. Lamar, C. Stuart Patterson, Bryant H. Prentice, III, and Mary Jane Taylor (1965), "Osmotic Properties Of Some Aqueous Solutions At 45 C", *Journal of Chemical & Engineering Data*, Vol. 10, No. 4, October, pp. 323-325.
- Holmes, H.F., C.F. Baes, Jr., and Robert E. Mesmer (1978), "Isopiestic Studies Of Aqueous Solutions At Elevated Temperatures I. KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>", *Journal of Chemical Thermodynamics*, Vol. 10, No. 10, pp. 983-996.
- Holmes, H.F. and Robert E. Mesmer (1983), "Thermodynamic Properties of Aqueous Solutions of the Alkali Metal Chlorides to 250 C", *Journal of Physical Chemistry*, Vol. 87, No. 7, pp. 1242-1255.
- Holmes, H.F., R.H. Busey, John M. Simonson, Robert E. Mesmer, D.G. Archer, and R.H. Wood (1987), "The Enthalpy Of Dilution Of HCl(aq) To 648 K And 40 MPa: Thermodynamic Properties", *Journal of Chemical Thermodynamics*, Vol. 19, pp. 863-890.
- Hood, G.C., O. Redlich, and C.A. Reilly (1954), "Ionization of Strong Electrolytes. III. Proton Magnetic Resonance in Nitric, Perchloric, and Hydrochloric Acids", *Journal of Chemical Physics*, Vol. 22, No. 12, December, pp. 2067-2071.
- Hood, G.C. and C.A. Reilly (1960), "Ionization of Strong Electrolytes. VIII. Temperature Coefficient of Dissociation of Strong Acids by Proton Magnetic Resonance", *Journal of Chemical Physics*, Vol. 32, No. 1, January, pp. 127-130.
- Humphries, William T., Carl F. Kohrt, and C. Stuart Patterson (1968), " Osmotic Properties of Some Aqueous Electrolytes at 60 C ", *Journal of Chemical & Engineering Data*, Vol. 13, No. 3, July, pp. 327-330.
- Iliuta, Maria C., Kaj Thomsen, and Peter Rasmussen (2002), "Modeling of Heavy Metal Salt Solubility Using the Extended UNIQUAC Model", *AIChE Journal*, Vol. 48, No. 11, November, pp. 2664-2689.
- International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. III, Edward W. Washburn, Clarence J. West, N. Ernest Dorsey, F.R. Bichowsky, and Alfons Klemenc Editors, McGraw-Hill Book Company, Inc.: New York, 1928.
- Jiang, Chengfa (1996a), "Activity Coefficients of Hydrochloric Acid in Concentrated Electrolyte Solutions. 1. HCl + NaCl + H<sub>2</sub>O, HCl + LiCl + H<sub>2</sub>O, and HCl + BaCl<sub>2</sub> + H<sub>2</sub>O at 298.15 K", *Journal of Chemical & Engineering Data*, Vol. 41, No. 1, pp. 113-116.
- Jiang, Chengfa (1996b), "Activity Coefficients of Hydrochloric Acid in Concentrated Electrolyte Solutions. 2. HCl + BaCl<sub>2</sub> + KCl + H<sub>2</sub>O, HCl + LiCl + KCl + H<sub>2</sub>O, and HCl + NaCl + KCl + H<sub>2</sub>O at 298.15 K", *Journal of Chemical & Engineering Data*, Vol. 41, No. 1, pp. 117-120.
- Krawetz, Arthur A. (1955), "A Raman Spectral Study of Equilibria in Aqueous Solutions of Nitric Acid", Ph.D. Theses, The University of Chicago, December.
- Linke, W.F. and A. Seidell (1965), *Solubilities of Inorganic and Metal-Organic Compounds*, 4<sup>th</sup> Edition, Vol. II, American Chemical Society: Washington, D.C.

- Lu, Xiaohua, Luzheng Zhang, Yanru Wang, Jun Shi, and Gerd Maurer (1996), "Prediction of Activity Coefficients of Electrolytes in Aqueous Solutions at High Temperature", *Industrial & Engineering Chemistry Research*, Vol. 35, No. 5, May, pp. 1777-1784.
- Lukas, Michael and Dirk M. Eden (1995), "Improved Representation of the Vapor-Liquid Equilibrium of HCl-H<sub>2</sub>O", *AIChE Journal*, Vol. 41, No. 4, April, pp. 1041-1043.
- Macaskill, J.B., Robert A. Robinson, and Roger G. Bates (1977), "Activity Coefficient of Hydrochloric Acid in Aqueous Solutions of Sodium Chloride", *Journal of Solution Chemistry*, Vol. 6, No. 6, pp. 385-392.
- Macaskill, J.B. and Roger G. Bates (1978), "Activity Coefficient of Hydrochloric Acid in the System HCl-KCl at 25° C and Ionic Strengths from 0.1 to 3 Moles/kg", *Journal of Solution Chemistry*, Vol. 7, No. 6, pp. 433-442.
- Macaskill, J.B., Carmen A. Vega, and Roger G. Bates (1978), "Activity Coefficients of Hydrochloric Acid in HCl-KCl-H<sub>2</sub>O Mixtures at Ionic Strengths up to 1.5 mol kg<sup>-1</sup> and Temperatures from 5 to 45 °C", *Journal of Chemical and Engineering Data*, Vol. 23, No. 4, October, pp. 314-316.
- Marshall, William L. and Ruth Slusher (1975), "The Ionization Constant Of Nitric Acid At High Temperatures From Solubilities Of Calcium Sulfate In HNO<sub>3</sub>-H<sub>2</sub>O, 100-350° C; Activity Coefficients And Thermodynamic Functions", *Journal of Inorganic Nuclear Chemistry*, Vol. 37, No. 5, May, pp. 1191-1202.
- Marsh, A.R.W. and W.J. McElroy (1985), "The dissociation Constant And Henry's Law Constant Of HCl In Aqueous Solution", *Atmospheric Environment*, Vol. 19, No. 7, pp. 1075-1080.
- Moore, John T., William T. Humphries, and C. Stuart Patterson (1972), "Osmotic Behavior Of Aqueous Salt Solutions At Elevated Temperatures. Part IV", *Journal of Chemical & Engineering Data*, Vol. 17, No. 2, pp. 180-182.
- Nichols, Todd T., Charles M. Barnes, Lance Lauerhass, and Dean D. Taylor (2001), *Selection of Steady-State Process Simulation Software to Optimize Treatment of Radioactive and Hazardous Waste*, INEEL/EXT-01-00485, May.
- Nichols, Todd T. and Dean D. Taylor (2002), *Physical Properties Models For Simulaiton Of Processes To Treat INEEL Tank Farm Waste; Thermodynamic Equilibrium*, INEEL/EXT-02-00877, July.
- Pascal, P. and C.R. Garnier (1923), *Memor. Poud.*, Vol. 20, 39.
- Partanen, Jaakko I. and Arthur K. Covington (2002), "Re-Evaluation Of The Activity Coefficients Of Aqueous Hydrochloric Acid Solutions Up To A Molality Of 2.0 Using Two-Parameter Huckel And Pitzer Equations. Part II. Results From 0 To 95° C", *Journal of Solution Chemistry*, Vol. 31, No. 3, March, pp. 197-210.
- Perez-Villasenor, Fernando, Gustavo A. Iglesias-Silva, and Kenneth R. Hall (2002), "Osmotic And Activity Coefficients Using A Modified Pitzer Equation For Strong Electrolytes 1:1 and 1:2 at 298.15 K", *Industrial & Engineering Chemistry Research*, Vol. 41, No. 5, March 6, pp. 1031-1037.
- Perry, Robert H. and Don W. Green (1997), *Perry's Chemical Engineers' Handbook*, Seventh Edition, McGraw-Hill: San Francisco, CA.
- Pitzer, Kenneth S. (1973), "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations", *Journal of Physical Chemistry*, Vol. 77, No. 2, January 18, pp. 268-277.
- Pitzer, Kenneth S., Editor (1991), *Activity Coefficients in Electrolyte Solutions*, 2nd Edition, CRC Press: Ann Arbor.
- Pitzer, Kenneth S., Christopher Peiper, and R.H. Busey (1984), "Thermodynamic Properties of Aqueous Sodium Chloride", *Journal of Physical and Chemical Reference Data*, Vol. 13, No. 1, pp. 1-102.
- Potier (1957), "Etude Des Proprietes Thermodynamiques Des Systemes Acide Nitrique - Eau Et Peroxyde D'azote Acide Nitrique", *Annales De La Faculte des Sciences De L'universite De Toulouse Pour Les Sciences Mathematiques Et Les Sciences Physiques*, Vol. 20, pp. 1-98.  
Note: I have seen the year for this reference cited both as 1957 and 1956 - according to the volume's front page, Vol. 20 appears to correspond to the year 1956, and the volume appears to not have been published until 1957.
- Redlich, O., W.E. Gargrave, and W.D. Krostek (1968), "Thermodynamics of Solutions: Consistency

- of Sparse Data. Activities of Nitric and Perchloric Acids", *Industrial and Engineering Chemistry Fundamentals*, Vol. 7, No. 2, May, pp. 211-214.
- Robinson, R.A. (1936), "The Dissociation Constant Of Hydrochloric Acid", *Transactions of the Faraday Society*, Vol. 32, pp. 743-744.
- Robinson, R.A. and R.H. Stokes (1959), *Electrolyte Solutions: The Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in Solutions of Simple Electrolytes*, 2<sup>nd</sup> Edition, Academic Press, Inc.: New York.
- Sako, Takeshi, Toshikatsu Hakuta, and Hiroshi Yoshitome (1984), "Salt Effects On Vapor-Liquid Equilibria For Volatile Strong Electrolyte-Water Systems", *Journal of Chemical Engineering of Japan*, Vol. 17, No. 4, August, pp. 381-388.
- Sako, Takeshi, Toshikatsu Hakuta, and Hiroshi Yoshitome (1985), "Vapor Pressures of Binary (H<sub>2</sub>O-HCl, -MgCl<sub>2</sub>, and -CaCl<sub>2</sub>) and Ternary (H<sub>2</sub>O-MgCl<sub>2</sub>-CaCl<sub>2</sub>) Aqueous Solutions", *Journal of Chemical and Engineering Data*, Vol. 30, No. 2, pp. 224-228.
- Sampoli, M., A. De Santis, Nunziata C. Marziano, and A. Zingales (1985), "Equilibria of Nitric Acid in Sulfuric and Perchloric Acid at 25 C by Raman and UV Spectroscopy", *Journal of Physical Chemistry*, Vol. 89, No. 13, pp. 2864-2869.
- Schreinemakers, F.A.H. (1909-10), *Z. Physik. Chem.*, Vol. 68, pp. 83-103.
- Sillen, Lars Gunnar and Arthur E. Martell (1964), *Stability Constants Of Metal-Ion Complexes*, Special Publication No. 17, The Chemical Society: London.
- Sillen, Lars Gunnar and Arthur E. Martell (1971), *Stability Constants Of Metal-Ion Complexes: Supplement No. 1*, Special Publication No. 25, Supplement to Special Publication No. 17, The Chemical Society: London.
- Simonson, J.M., H.F. Holmes, R.H. Busey, R.E. Mesmer, D.G. Archer, and R.H. Wood (1990), "Modeling of the Thermodynamics of Electrolyte Solutions to High Temperatures Including Ion Association. Application to Hydrochloric Acid", *Journal of Physical Chemistry*, Vol. 94, No. 19, pp. 7675-7681.
- Snipes, H.P., C. Manly, and D.D. Ensor (1975), "Heats of Dilution of Aqueous Electrolytes: Temperature Dependence", *Journal of Chemical & Engineering Data*, Vol. 20, No. 3, pg. 287.
- Sproesser, William C. and Guy B. Taylor (1921), "Vapor Pressures Of Aqueous Solutions Of Nitric Acid", *Journal of the American Chemical Society*, Vol. 43, pp. 1782-1787.
- Sterner, S. Michael, Donald L. Hall, and Robert J. Bodnar (1988), "Synthetic Fluid Inclusions. V. Solubility Relations In The System NaCl-KCl-H<sub>2</sub>O Under Vapor-Saturated Conditions", *Geochimica et Cosmochimica Acta*, Vol. 52, pp. 989-1005.
- Tang, I.N., H.R. Munkelwitz, and J.H. Lee (1988), "Vapor-Liquid Equilibrium Measurements For Dilute Nitric Acid Solutions", *Atmospheric Environment*, Vol. 22, No. 11, pp. 2579-2585.
- Taylor, Dean D. and Todd T. Nichols (2003), *Revised Computer Program To Regress Parameters For Pitzer's Model*, INEEL/EXT-03-01146, September.
- Weber, Charles F. (2000), "Calculation Of Pitzer Parameters At High Ionic Strengths", *Industrial & Engineering Chemistry Research*, Vol. 39, No. 11, November, pp. 4422-4426.
- Weber, Charles F., Edward C. Beahm, Douglas D. Lee, and Jack S. Watson, (2000), "A Solubility Model For Aqueous Solutions Containing Sodium, Fluoride, And Phosphate Ions", *Industrial & Engineering Chemistry Research*, Vol. 39, No. 2, February, pp. 518-526.
- Yakimov, M.A. and V.Ya. Mishin, (1964), "Calculation Of Pitzer Parameters At High Ionic Strengths", *Soviet Radiochemistry*, Vol. 6, No. 5, pp. 523-527.
- Zemaitis, Joseph F., Jr., Diane M. Clark, Marshall Rafal, and Noel C. Scrivner (1986), *Handbook of Aqueous Electrolyte Thermodynamics*, Design Institute for Physical Property Data, Sponsored by the American Institute of Chemical Engineers, Inc.: New York.

## **APPENDIX A: HENRY'S LAW FOR ACID GASES IN ASPEN PLUS**

## ***Introduction***

ASPEN Plus uses the rational symmetric convention for the solvents and the rational asymmetric convention for solutes when using Henry's law, regardless of the physical property method selected by the user. Consequently, the user has to assure that Henry's law constants used in the simulation are consistent with both the convention of the physical property method selected by the user and the rational asymmetric convention used internally by ASPEN Plus for Henry's law. The rational asymmetric convention uses the mole fraction concentration scale and has the reference state corresponding to the hypothetical ideal state of pure solute constrained by the condition that the activity coefficient of the solute has a value of one at infinite dilution at all temperatures. The rational symmetric convention uses the mole fraction scale and uses the pure-component reference state at all temperatures. The rational asymmetric and symmetric conventions are related by

$$\gamma_i^a = \frac{\gamma_i^s}{\gamma_i^{s,\infty}}, \quad [\text{A1}]$$

where  $\gamma_i^a$  is the activity coefficient of solute  $i$  on the rational asymmetric convention,  $\gamma_i^s$  is solute  $i$ 's activity coefficient on the rational symmetric convention, and  $\gamma_i^{s,\infty}$  is the value of the solute's rational symmetric activity coefficient at infinite dilution. Thus, Henry's law is expressed by

$$p_i = x_i \gamma_i^a H_i = x_i \frac{\gamma_i^s}{\gamma_i^{s,\infty}} H_i, \quad [\text{A2}]$$

where  $H_i$  is the Henry's law constant (units of atm) used by ASPEN Plus in its internal calculations for thermodynamic equilibrium of volatile solute  $i$  (Aspen Technologies, 2001; Iliuta et al., 2002).

ASPEN Plus also multiplies the Henry's law constant by a pressure correction term which is not shown in Eq. [A2] because its impact at atmospheric pressure and low temperatures is negligible. The correction term was not used when regressing our Henry's law constants, and therefore, it is not relevant to this discussion. Eq. [A2] expresses the partial pressure for solute  $i$  as a function of the mole fraction of associated solute in the liquid phase, the Henry's law constant, and the rational activity coefficient in both the symmetric and asymmetric conventions.

## ***Compatibility With the Reference State Convention of the Pitzer Model***

A relationship between the rational symmetric convention of ASPEN Plus and the practical electrolyte convention of the Pitzer model can be easily developed by following the logic given by Denbigh (1981, pp. 275-278). We have

$$\left. \begin{aligned} \mu_i &= \mu_i^{\circ,s} + RT \ln \gamma_i^s x_i \\ \mu_i &= \mu_i^{\circ} + RT \ln \gamma_i m_i \end{aligned} \right\} \quad [\text{A3}]$$

for the chemical potential of solute  $i$  in the two conventions. The value of the chemical potential is irrespective of the reference state, and so

$$RT \ln \frac{\gamma_i m_i}{\gamma_i^s x_i} = \mu_i^{\circ,s} - \mu_i^{\circ}. \quad [\text{A4}]$$

Under limiting conditions of infinite dilution  $m_i \rightarrow \frac{x_i}{M_o}$ ,  $\gamma_i \rightarrow 1$ , and  $\gamma_i^s \rightarrow \gamma_i^{s,\infty}$ , where  $M_o$  is the molar mass of the solvent (kg/mole), and Eq. [A4] reduces to

$$RT \ln \frac{1}{\gamma_i^{s,\infty} M_o} = \mu_i^{\circ,s} - \mu_i^{\circ}. \quad [\text{A5}]$$

The values of the standard state chemical potentials ( $\mu_i^{\circ,s}$  and  $\mu_i^{\circ}$ ) are independent of solution composition, and so the numerical value of their difference has precisely the same value in the general case (Eq. [A4]) as in the infinitely dilute case (Eq. [A5]). Consequently,

$$\frac{\gamma_i m_i}{\gamma_i^s x_i} = \frac{1}{\gamma_i^{s,\infty} M_o} \quad [\text{A6}]$$

$$M_o \gamma_i m_i = \frac{\gamma_i^s x_i}{\gamma_i^{s,\infty}}$$

and Eq. [A2] can be expanded to include the practical electrolyte convention,

$$p_i = x_i \gamma_i^a H_i = x_i \frac{\gamma_i^s}{\gamma_i^{s,\infty}} H_i = M_o \gamma_i m_i H_i \quad [\text{A2b}]$$

The Henry's law constant has the same value and units (atm) regardless of the convention chosen in the equalities of Eq. [A2b]. Henry's law constants regressed from solute partial pressure data with the Pitzer activity coefficient model according to the far right hand side of equality [A2b] is the form required for consistency with ASPEN Plus.

### ***Relationship To Form Based On Complete Dissociation***

It is also common to use a Henry's law for strong acids based on complete dissociation (Clegg & Brimblecombe, 1988a, 1988b, 1990; Carslaw et al., 1995). The activity in the liquid phase is that of the component ions rather than the associated solute. Although this doesn't introduce theoretical inexactitude, this form is not directly usable with ASPEN Plus because the software only uses Henry's law for electrically neutral species in solution. The relationship between the two forms is simple, however, and one can be derived from the other.

The form assuming complete dissociation into the component cation and anion is expressed as

$$H_i^d = \frac{(\gamma_+ m_+)^{v_+} (\gamma_- m_-)^{v_-}}{p_i} \quad [\text{A7}]$$

where superscript  $d$  on the Henry's law constant indicates the form based on complete dissociation ( $\text{mol}^2 \cdot \text{kg}^2 \cdot \text{atm}^{-1}$ ). The ionic molalities and activity coefficients are stoichiometric values because association is ignored. However, the numerator has the same value whether the values are stoichiometric or true (see Eq. [F]), and so this form can also be expressed as

$$H_i^d = \frac{K_d \gamma_i m_i}{p_i} \quad [\text{A8}]$$

where  $K_d$  is the molality-based, thermodynamic, dissociation constant, and  $\gamma_i m_i$  refers to the associated solute in the liquid phase. Substitute  $H_i M_o = \frac{p_i}{\gamma_i m_i}$  from Eq. [A2b], and one obtains

$$H_i = \frac{K_d}{H_i^d M_o} \quad [\text{A9}]$$

Eq. [A9] allows values of  $H_i$  for use in ASPEN Plus to be derived from values of  $H_i^d$  and  $K_d$ , and vice versa.

Figure 1. Harned & Owen vs. Akerlof & Teare Activity Coefficient Data For Aqueous HCl.

**Consistency of HCl Activity Coefficient Data (@20 C)**

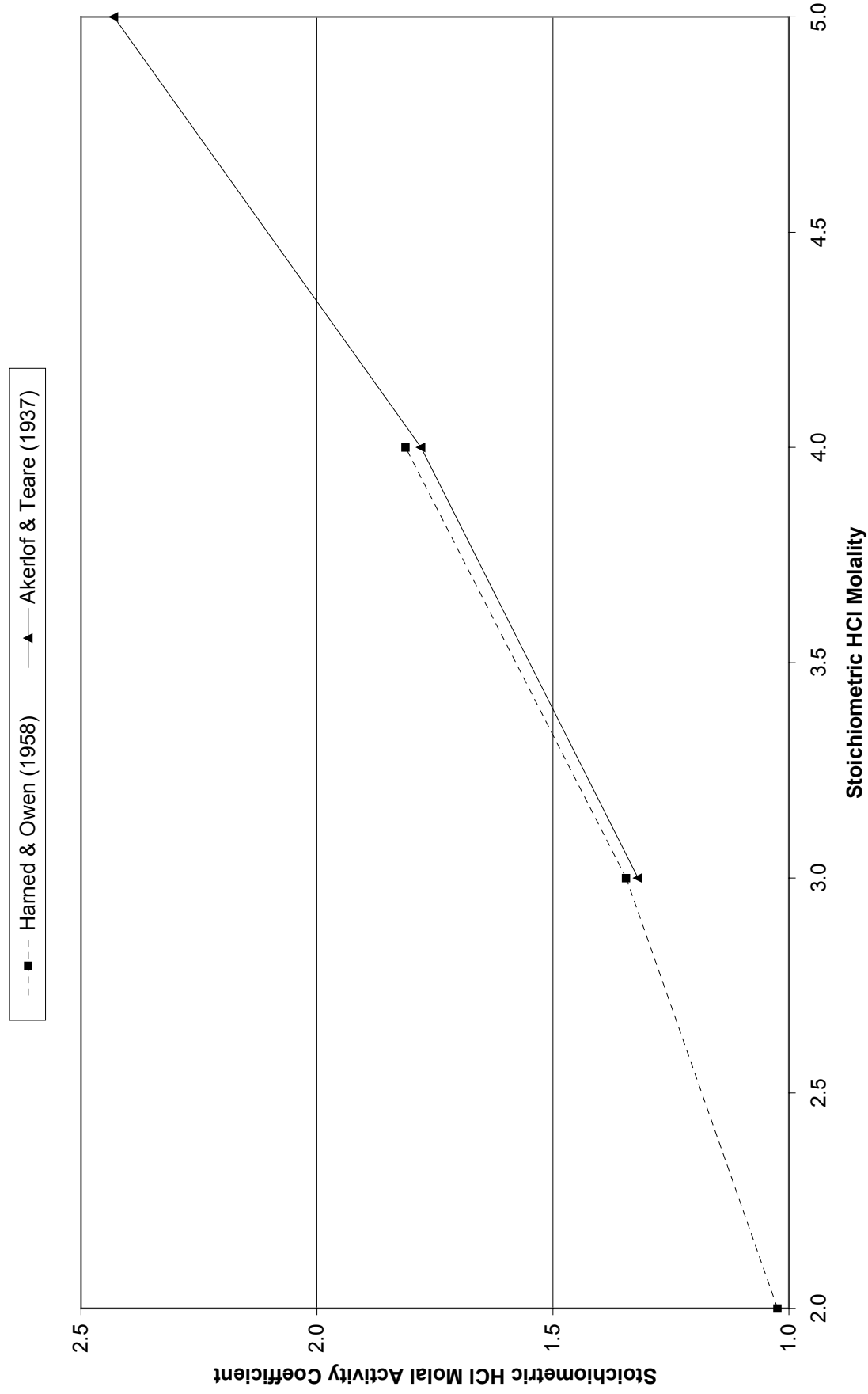




Figure 2. Comparison Of Osmotic Coefficients Calculated From Akerlof & Teare Water Activity Data For Aqueous HCl.

Consistency of Osmotic Coefficient Data For Aqueous HCl

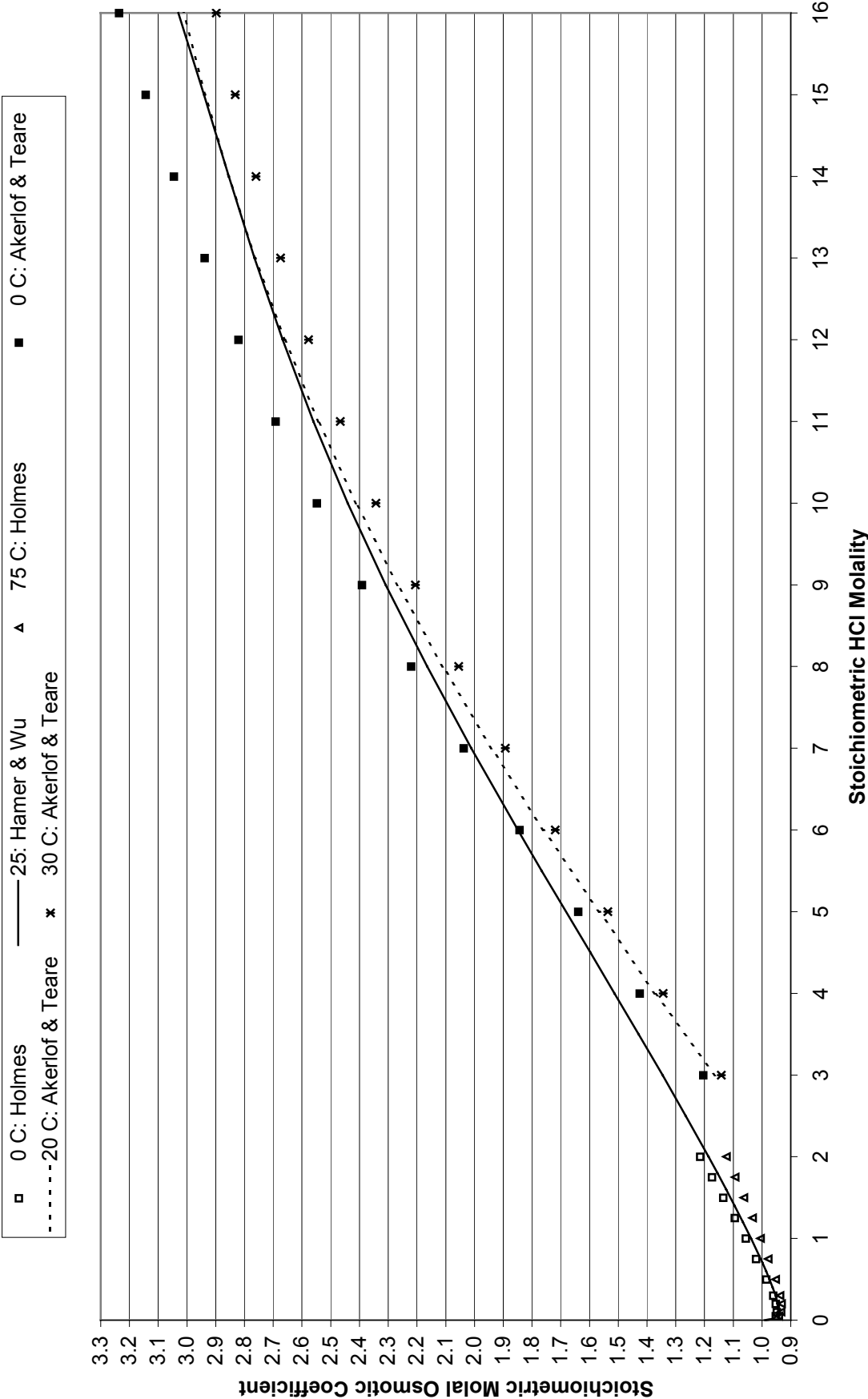


Figure 3. Assessment Of Impact Of High-Molality Activity Coefficient Data Of Cerquetti et al. (1968) On  $\lambda_{(\text{HCl}, \text{HCl})}$  @70 and 80° C.

### Lamda (HCl, HCl)

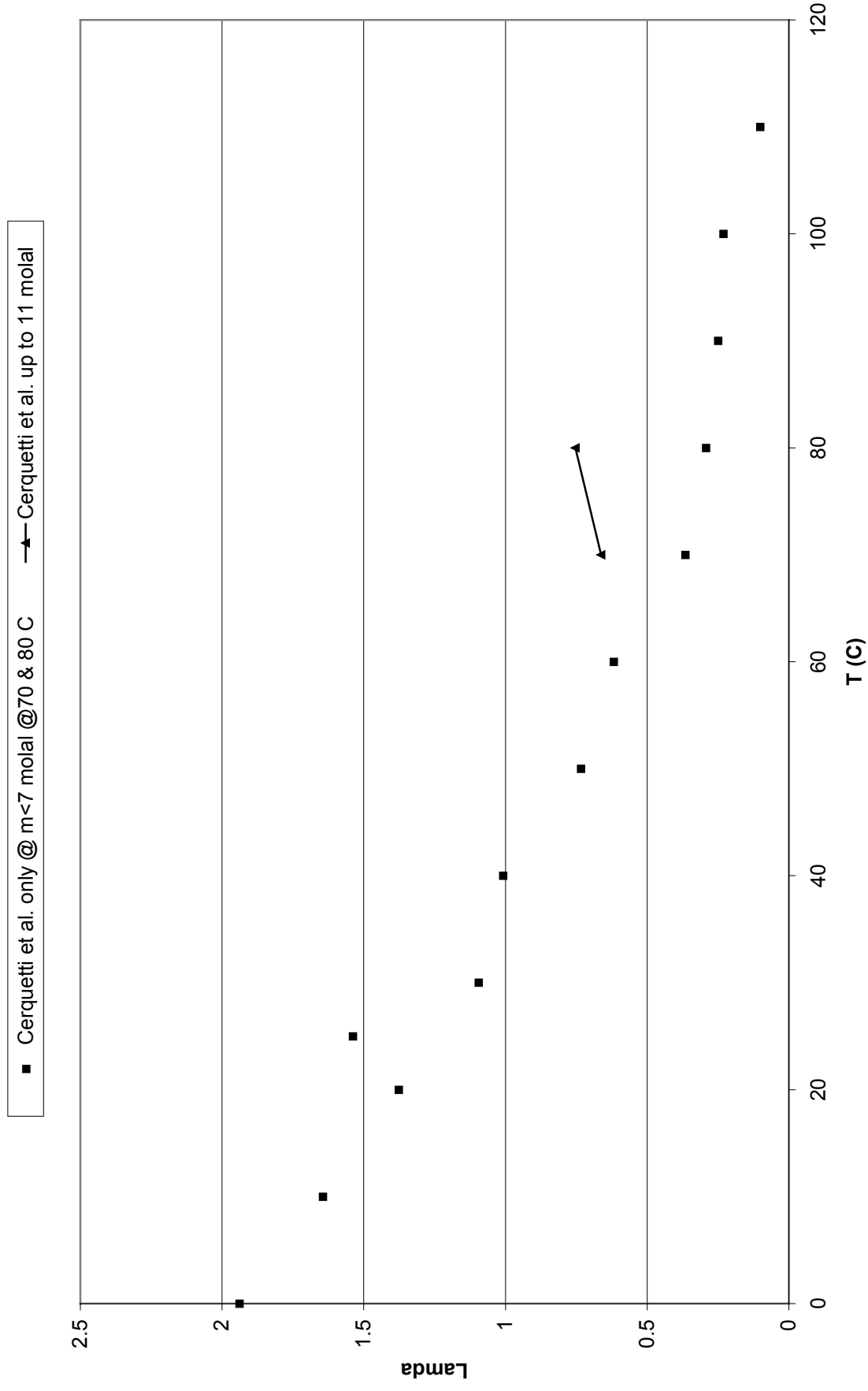


Figure 4. Assessment Of Impact Of High-Molality Activity Coefficient Data Of Cerquetti et al. (1968) On ( $\lambda_{\text{HCl, Cl}^-} + \lambda_{\text{HCl, H}^+}$ ) @70 and 80° C.

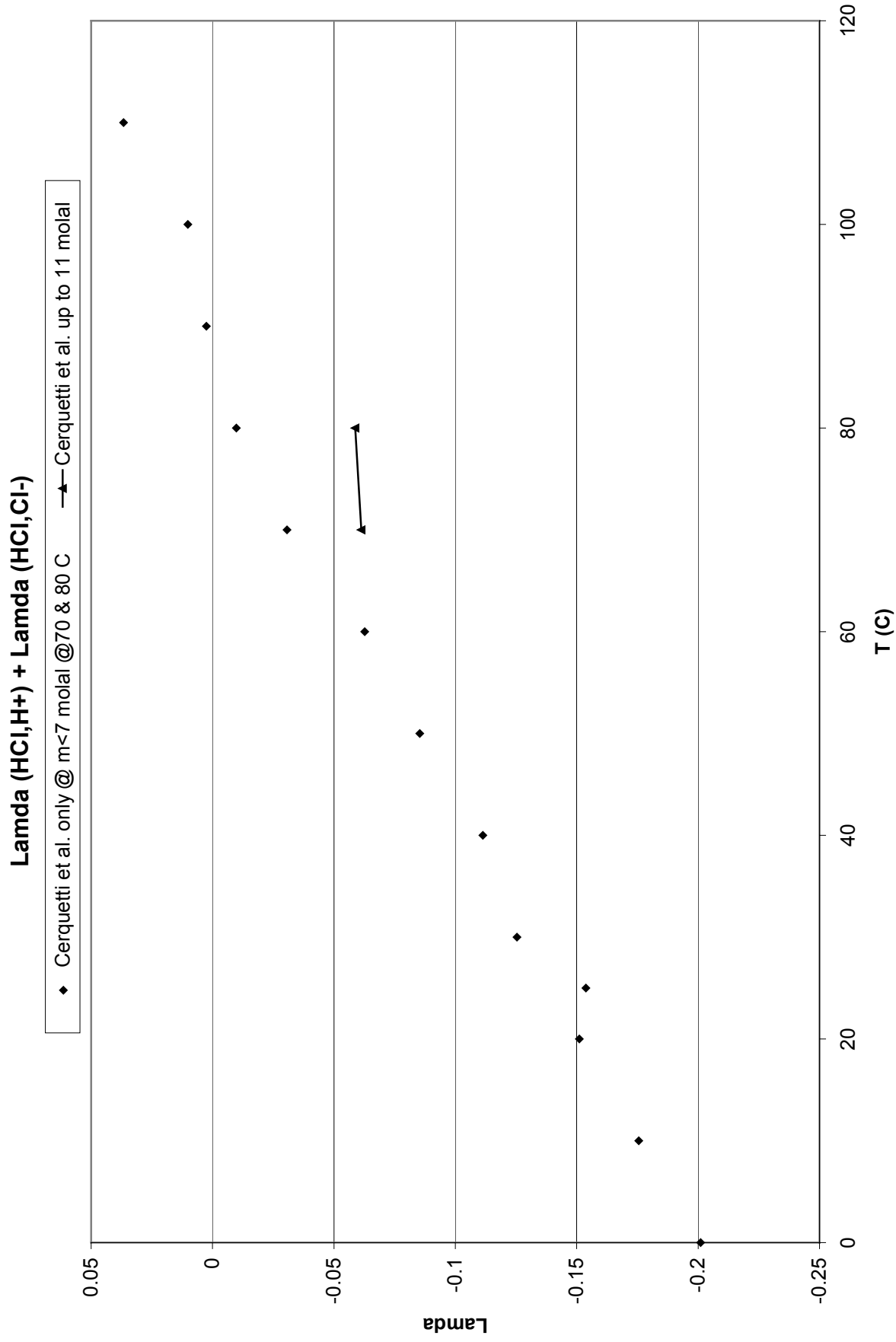


Figure 5. Comparison Between Regressed HCl Activity Coefficient Data And Model Predictions.

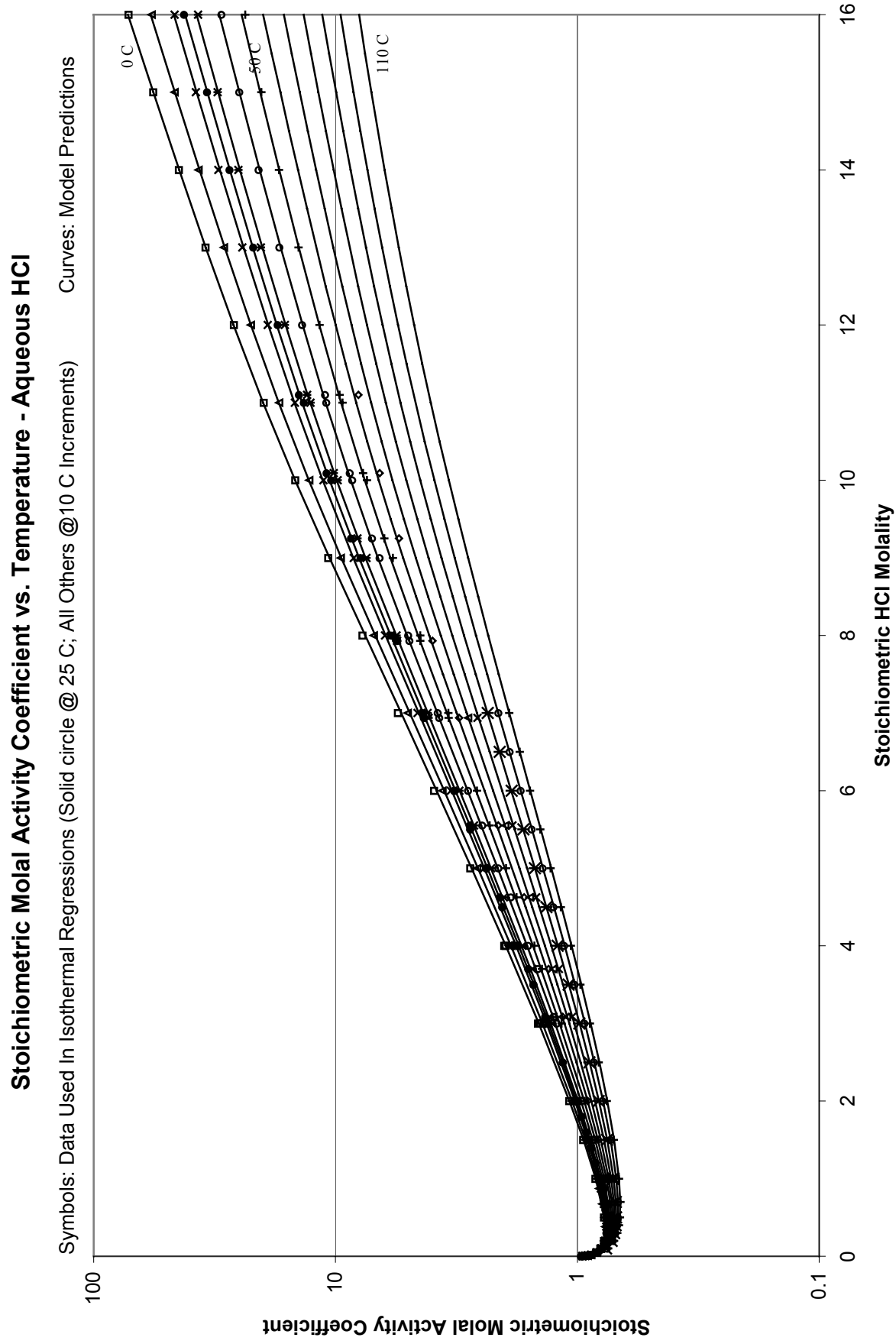


Figure 6. Comparison Between Regressed Osmotic Coefficient Data And Model Predictions

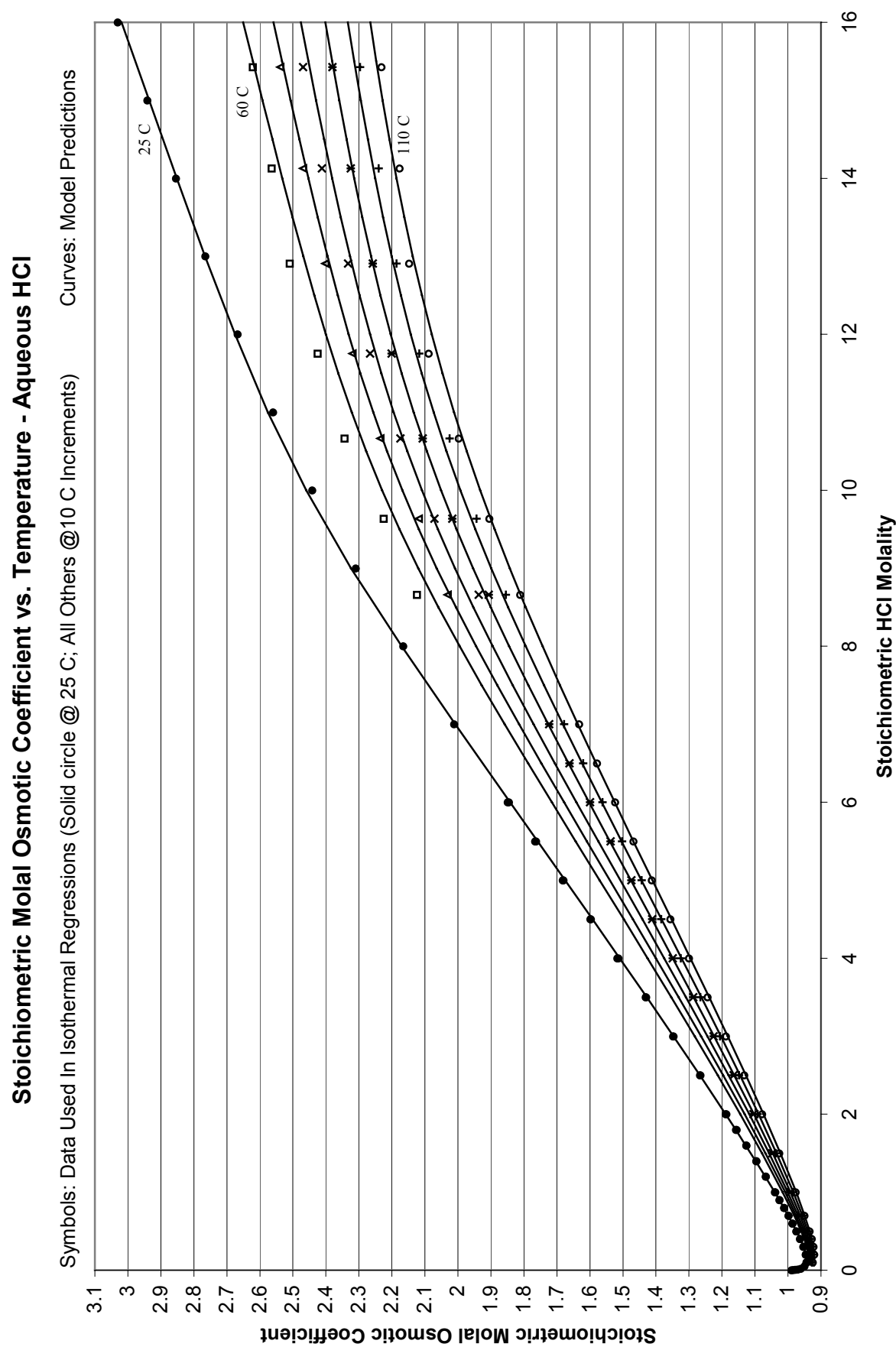


Figure 7. Comparison Between Model Predictions Of HCl Activity Coefficients And Low-Molality Data Not Used To Regress Pitzer Parameters.

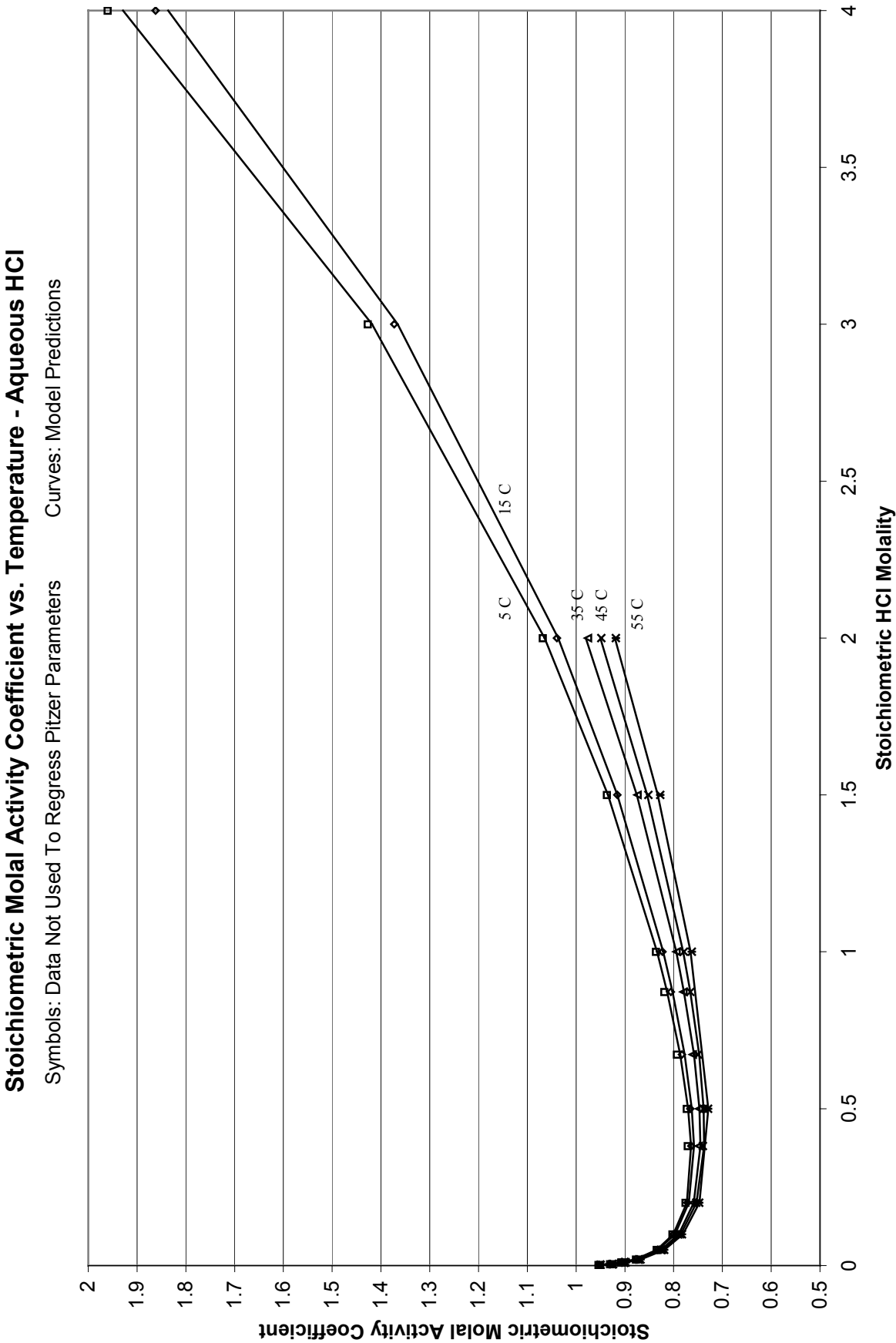


Figure 8. Comparison Between Model Predictions Of HCl Activity Coefficients And High-Molality Data Not Used To Regress Pitzer Parameters.

**Stoichiometric Molal Activity Coefficient vs. Temperature - Aqueous HCl**

Symbols: Data Not Used To Regress Pitzer Parameters      Curves: Model Predictions

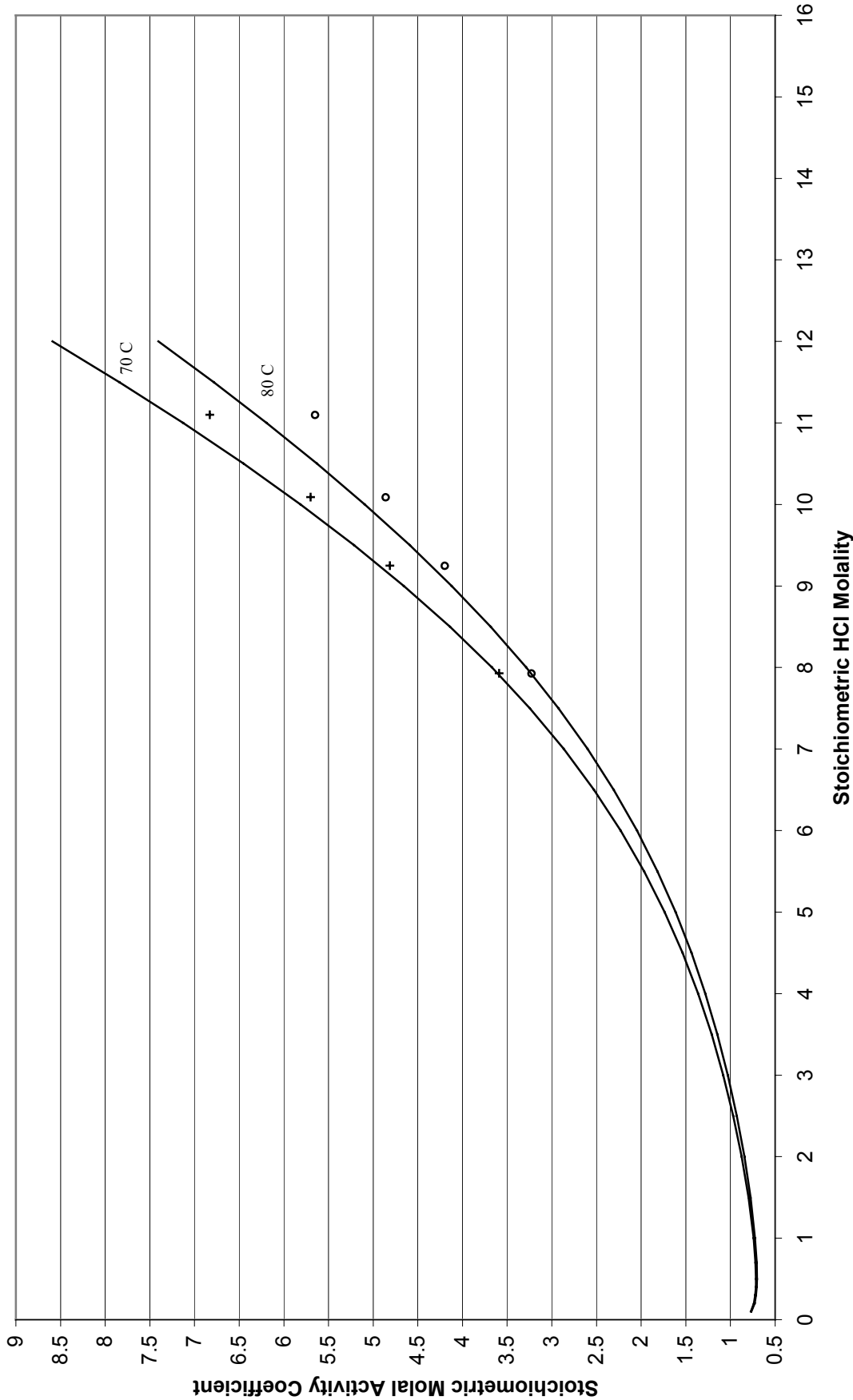


Figure 9. Predicted Extents of Dissociation of HCl in Water.

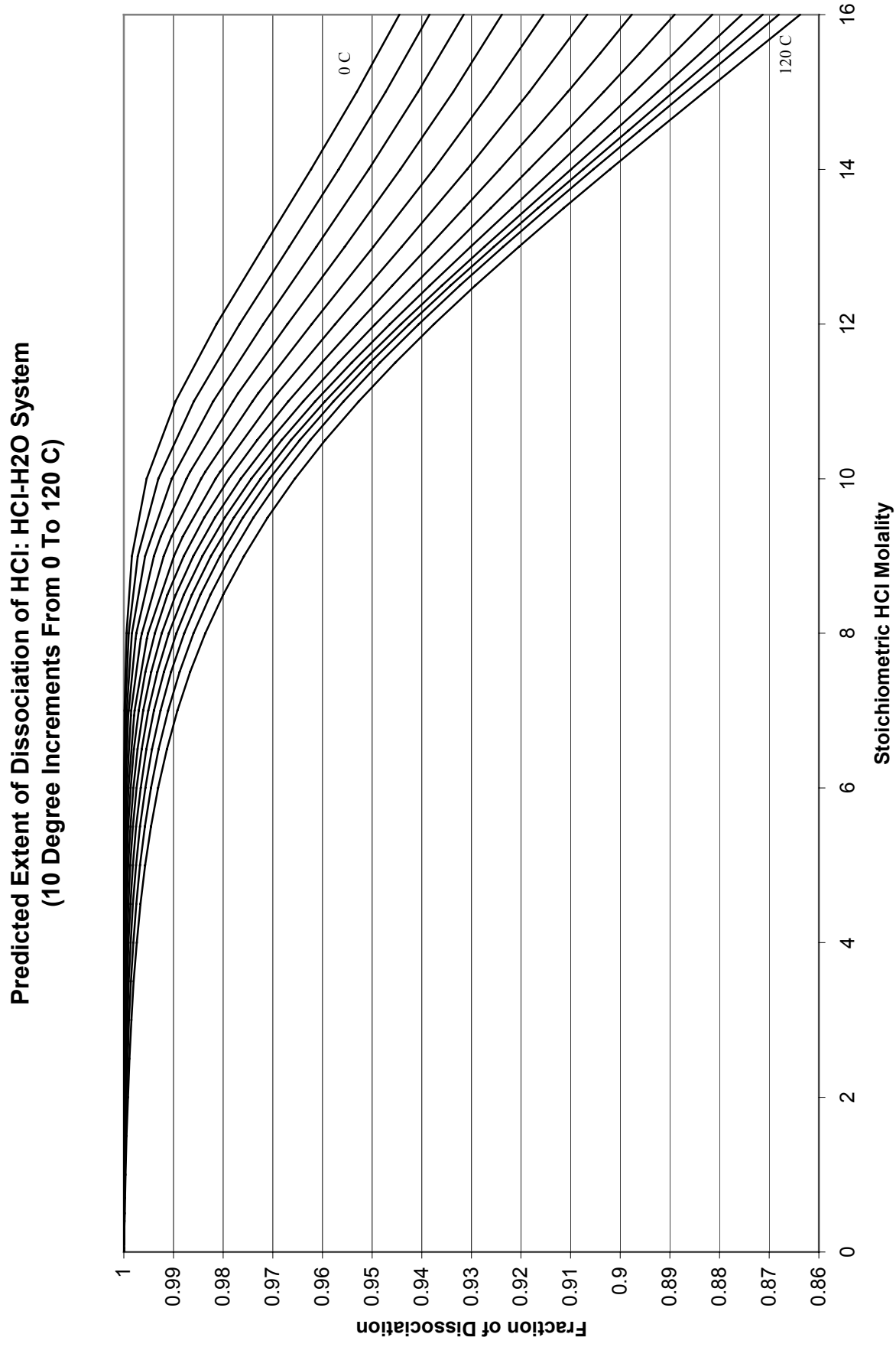




Figure 10. Predicted Molal Activity Coefficient of Associated HCl for HCl-H<sub>2</sub>O System.

**Predicted Molal Activity Coefficient of Associated Molecular HCl: HCl-H<sub>2</sub>O System  
(10 Degree Increments From 0 To 120 C)**

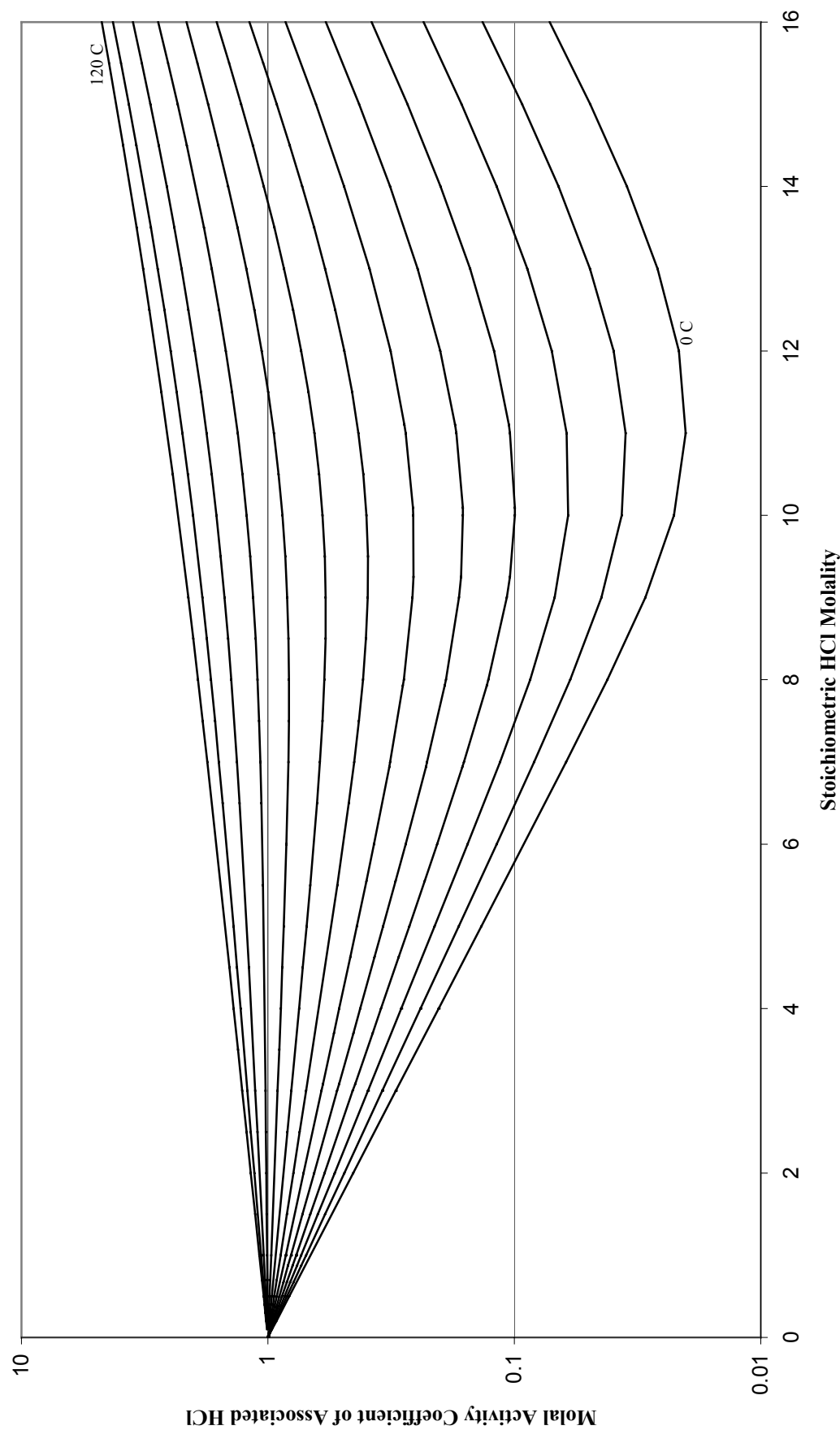


Figure 11. Comparison of Model vs. Data: HCl Partial Pressure for HCl-H<sub>2</sub>O System.

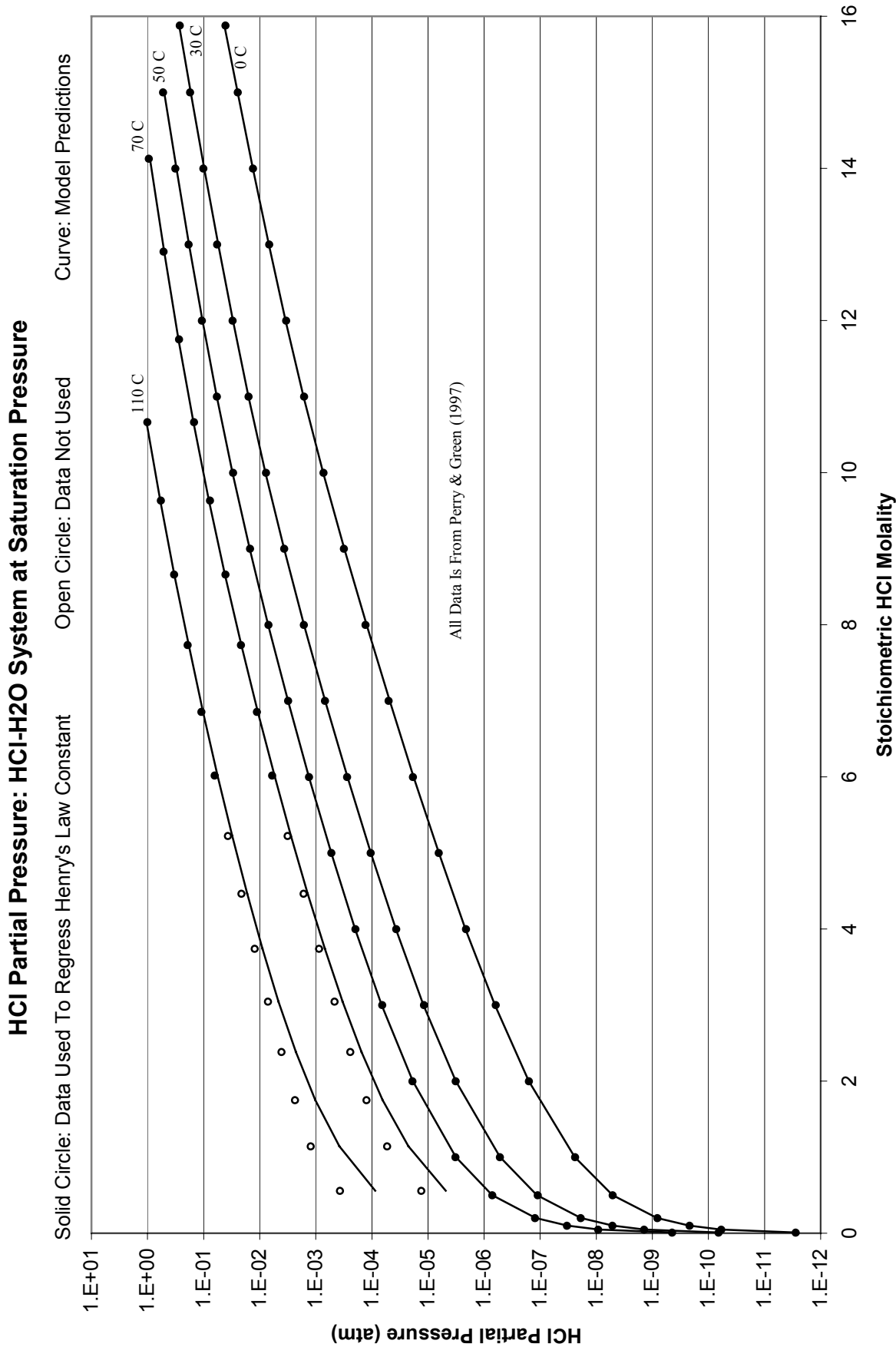


Figure 12. Comparison of Dissociation-Based Henry's Law Constants for HCl.

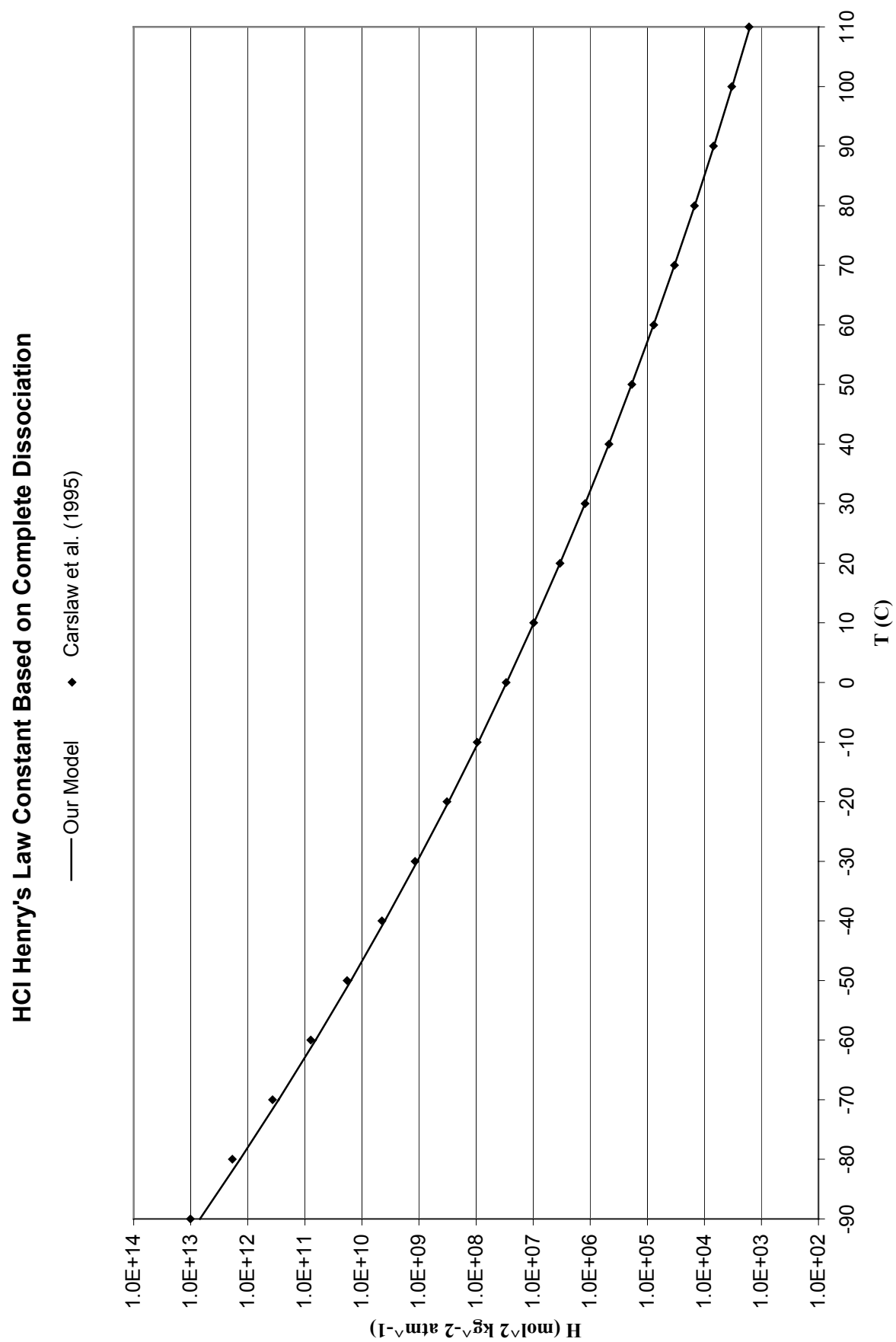


Figure 13. Recommended Correlation for Dissociation-Based Henry’s Law Constant (Eq. [13]) for HCl.

**HCl Henry's Law Constant Based on Complete Dissociation**

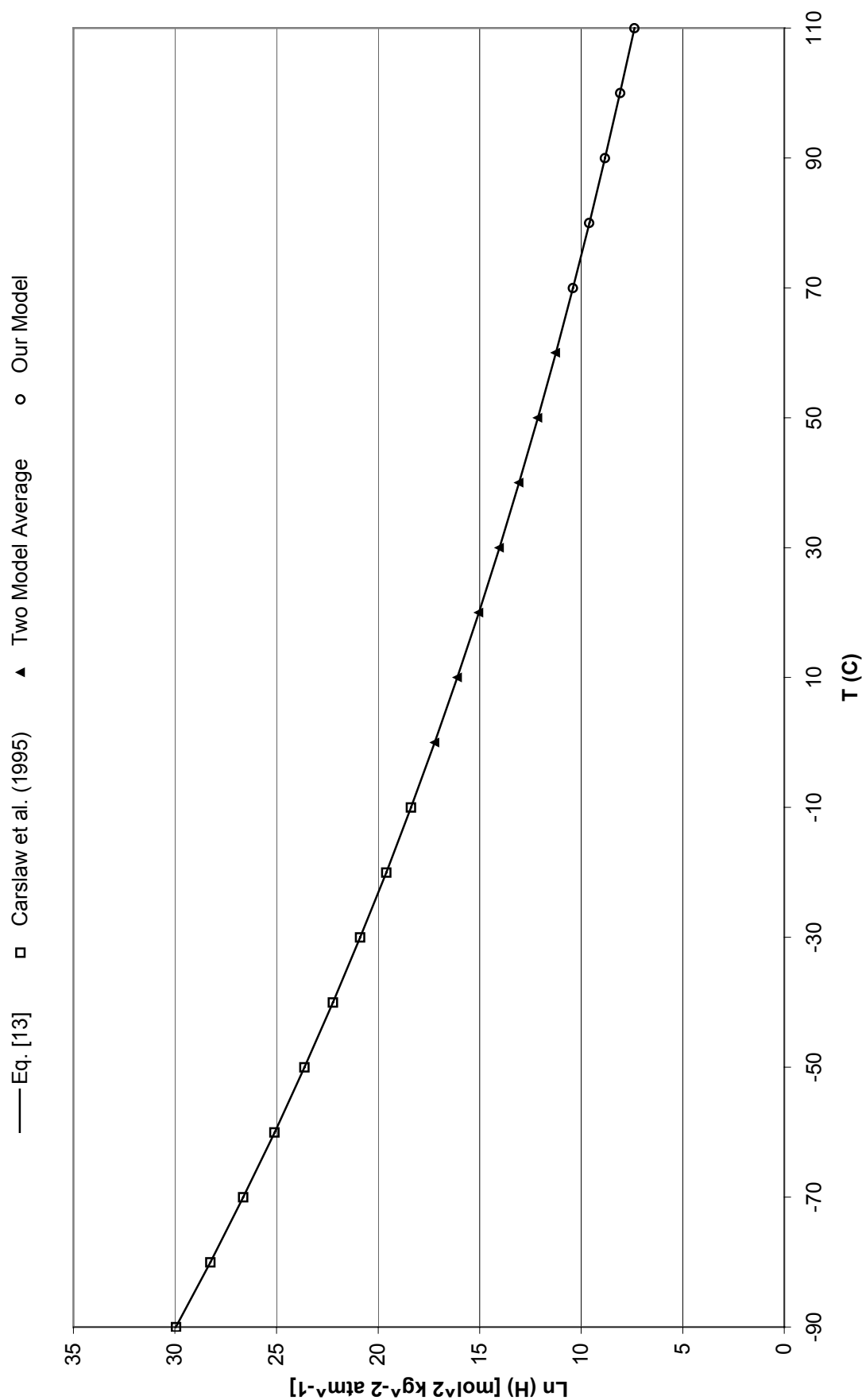


Figure 14. Experimental NaCl Solubility: HCl-NaCl-H<sub>2</sub>O @ 25° C.

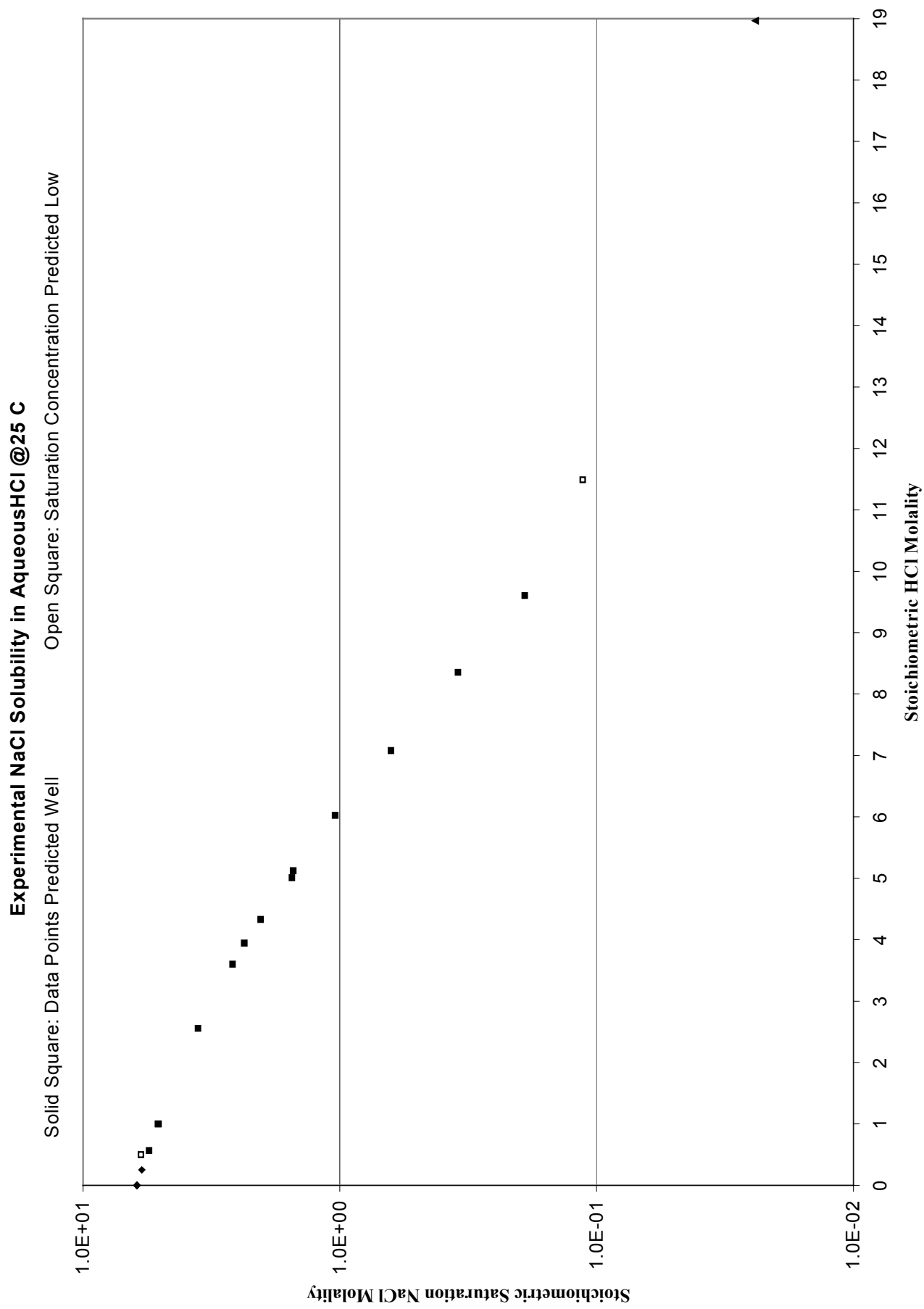


Figure 15. HCl Partial Pressure: HCl-KCl-NaCl-H<sub>2</sub>O System @25° C.

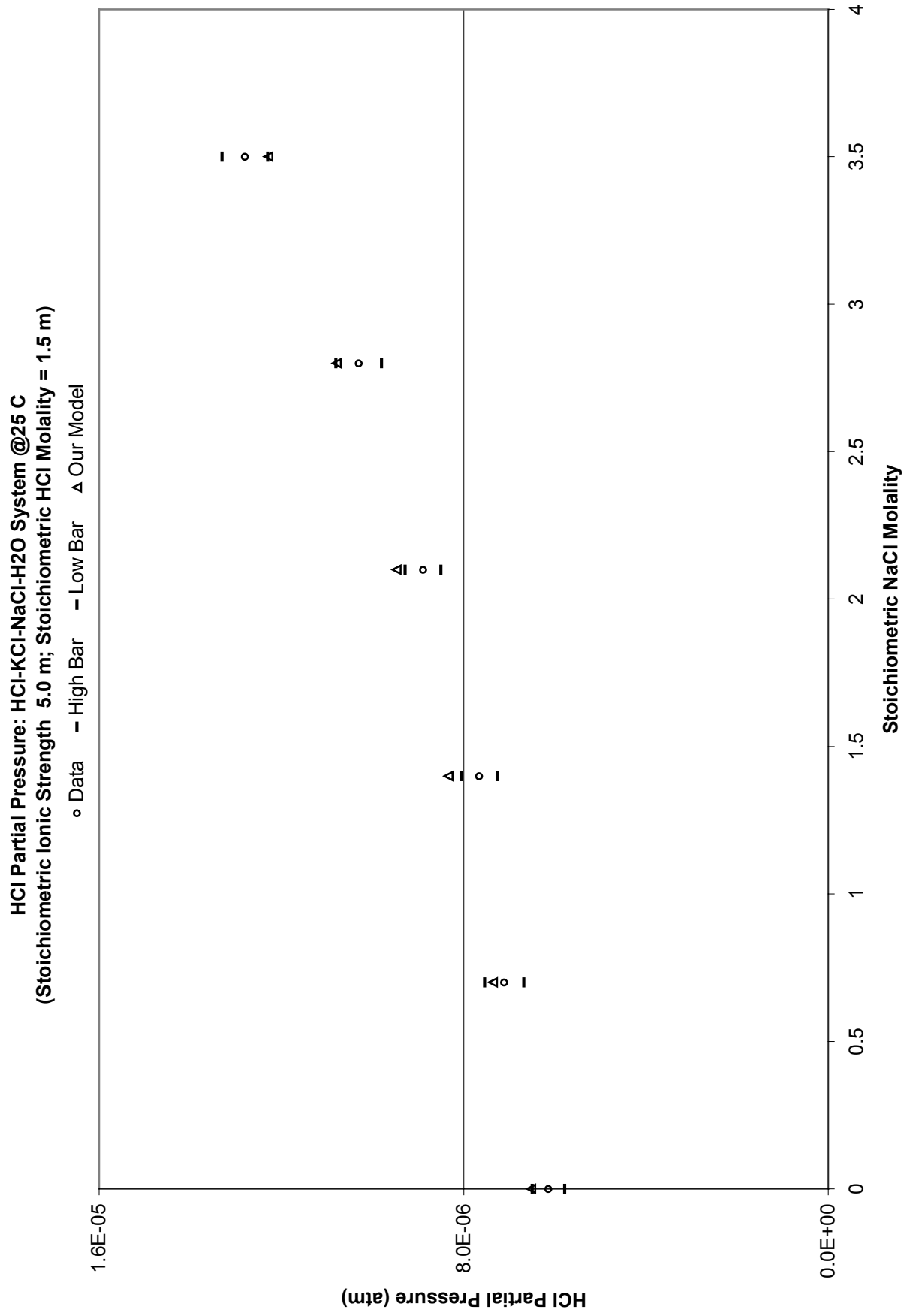


Figure 16. Variation From Constancy In The Saturation Ionic Product Of KCl @0° C Using Final Values For  $\theta_{H^+,K^+}$ ,  $\psi_{H^+,K^+,Cl^-}$ , and  $(\lambda_{(HCl, Cl^-)} + \lambda_{(HCl, K^+)})$ .

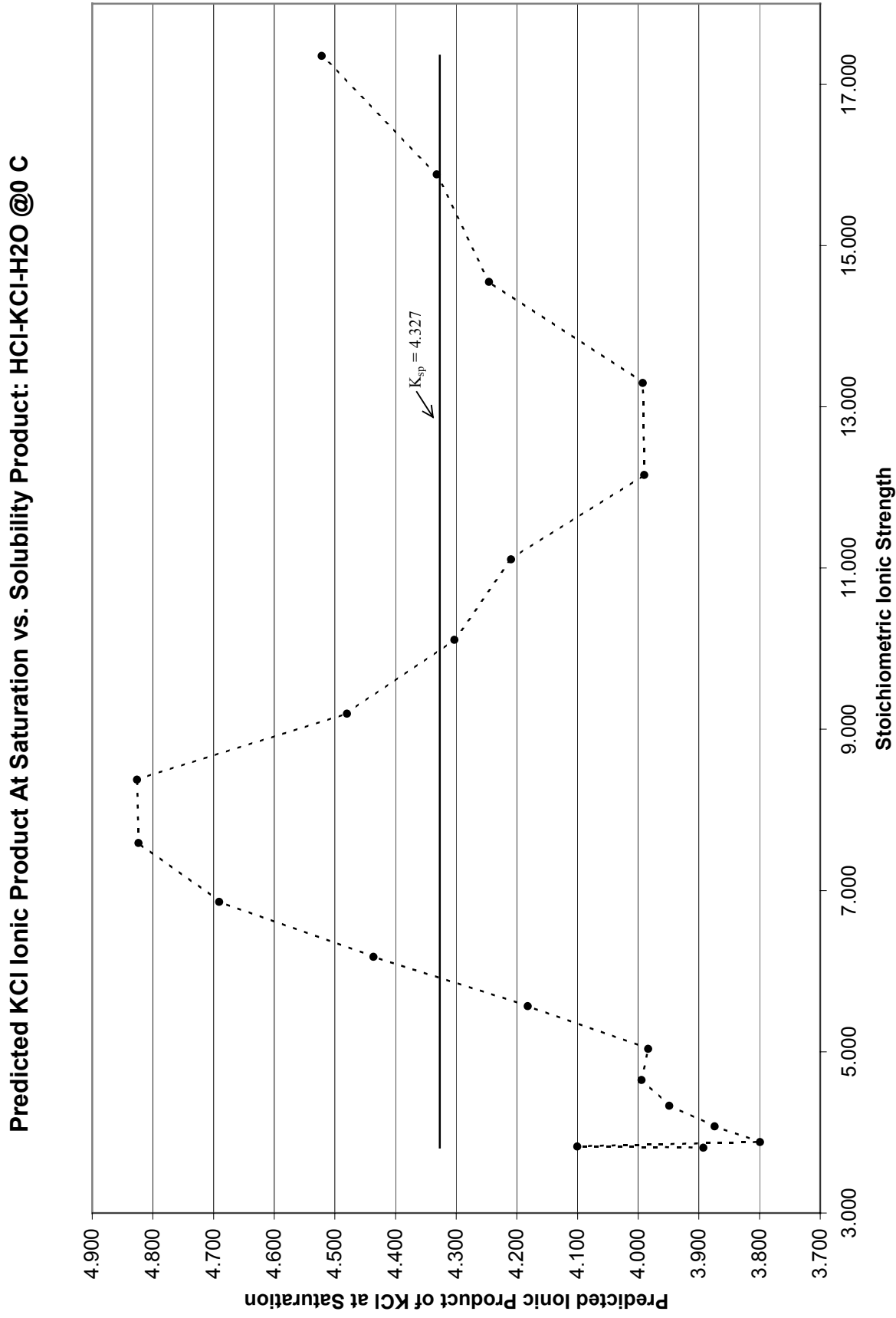


Figure 17. Variation From Constancy In The Saturation Ionic Product Of KCl @25° C Using Final Values For  $\theta_{H^+K^+}$ ,  $\Psi_{H^+K^+Cl^-}$  and  $(\lambda_{(HCl, Cl^-)} + \lambda_{(HCl, K^+)})$ .

### Predicted KCl Ionic Product At Saturation vs. Solubility Product: HCl-KCl-H2O @25 C

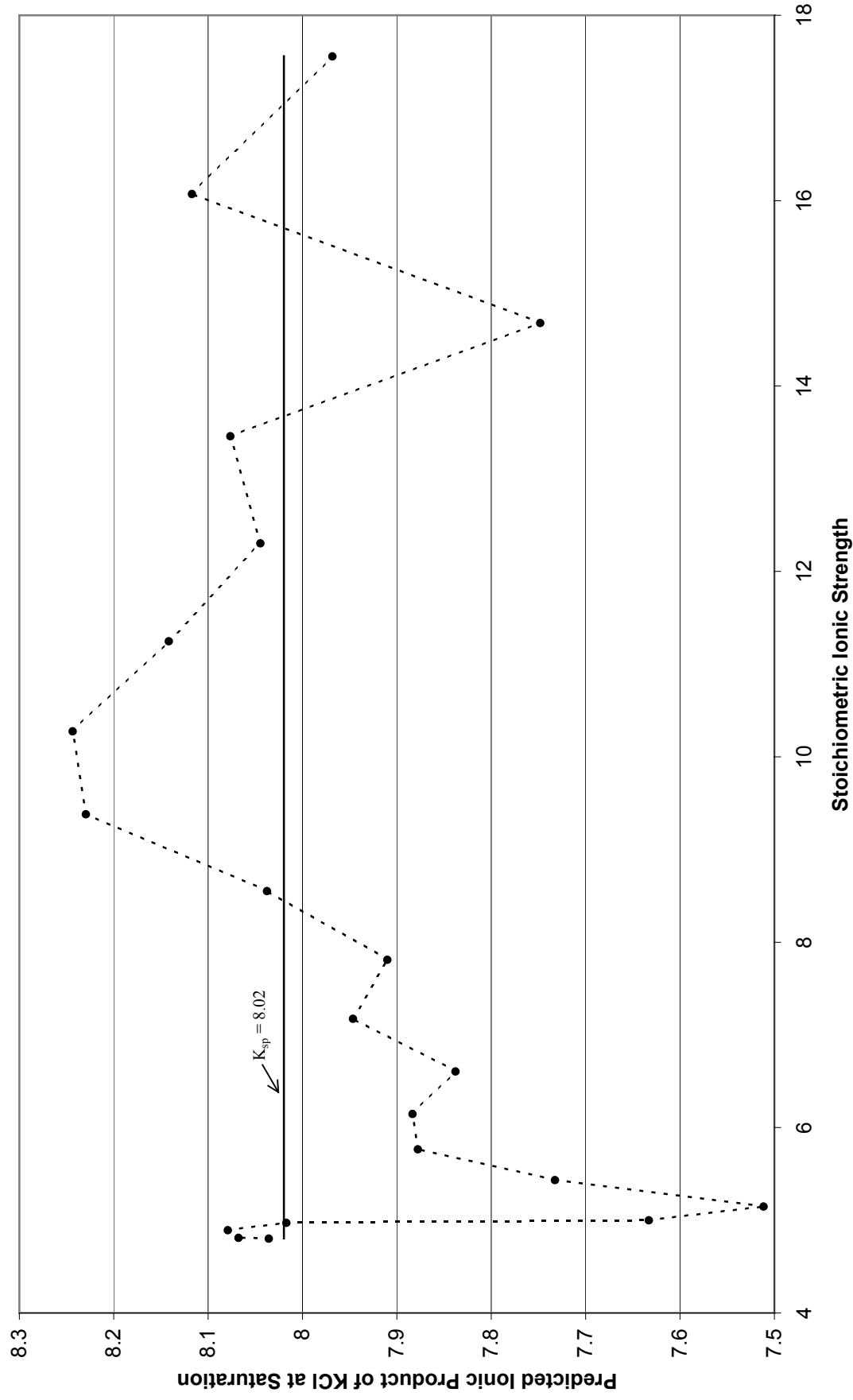




Figure 18. Pattern In Deviation of KCl Saturation Ionic Product @25° C Using Initial Values For  $\theta_{\text{H}^+, \text{K}^+}$ ,  $\psi_{\text{H}^+, \text{K}^+, \text{Cl}^-}$ , and  $(\lambda_{(\text{HCl}, \text{Cl}^-)} + \lambda_{(\text{HCl}, \text{K}^+)})$ .

### Predicted KCl Ionic Product At Saturation vs. Solubility Product: HCl-KCl-H2O @25 C

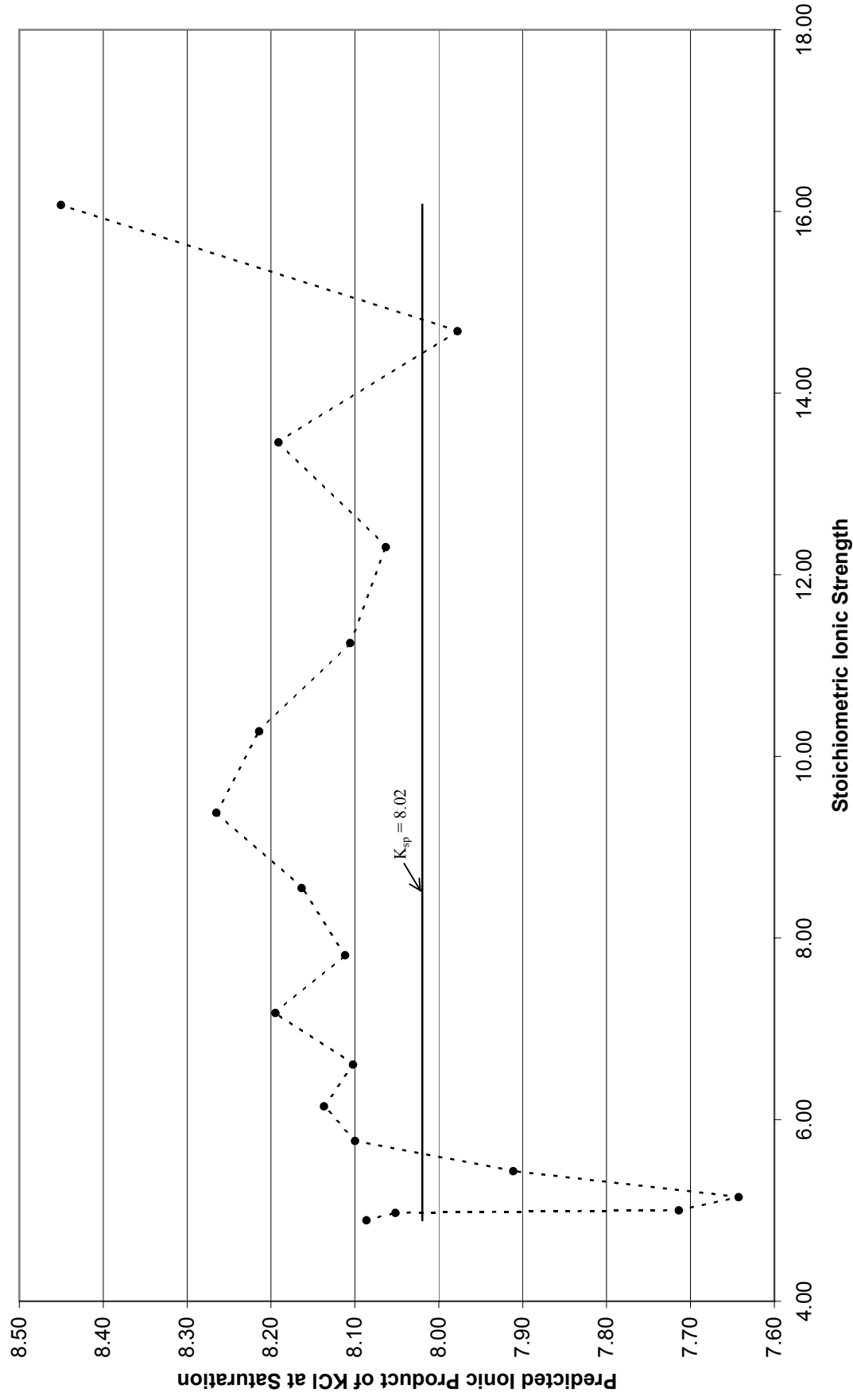


Figure 19. Comparison of Osmotic Coefficients Calculated From VLE Data:  $\text{HNO}_3\text{-H}_2\text{O}$  System @ 25° C.

### Osmotic Coefficient Comparison: $\text{HNO}_3\text{-H}_2\text{O}$ @25 C

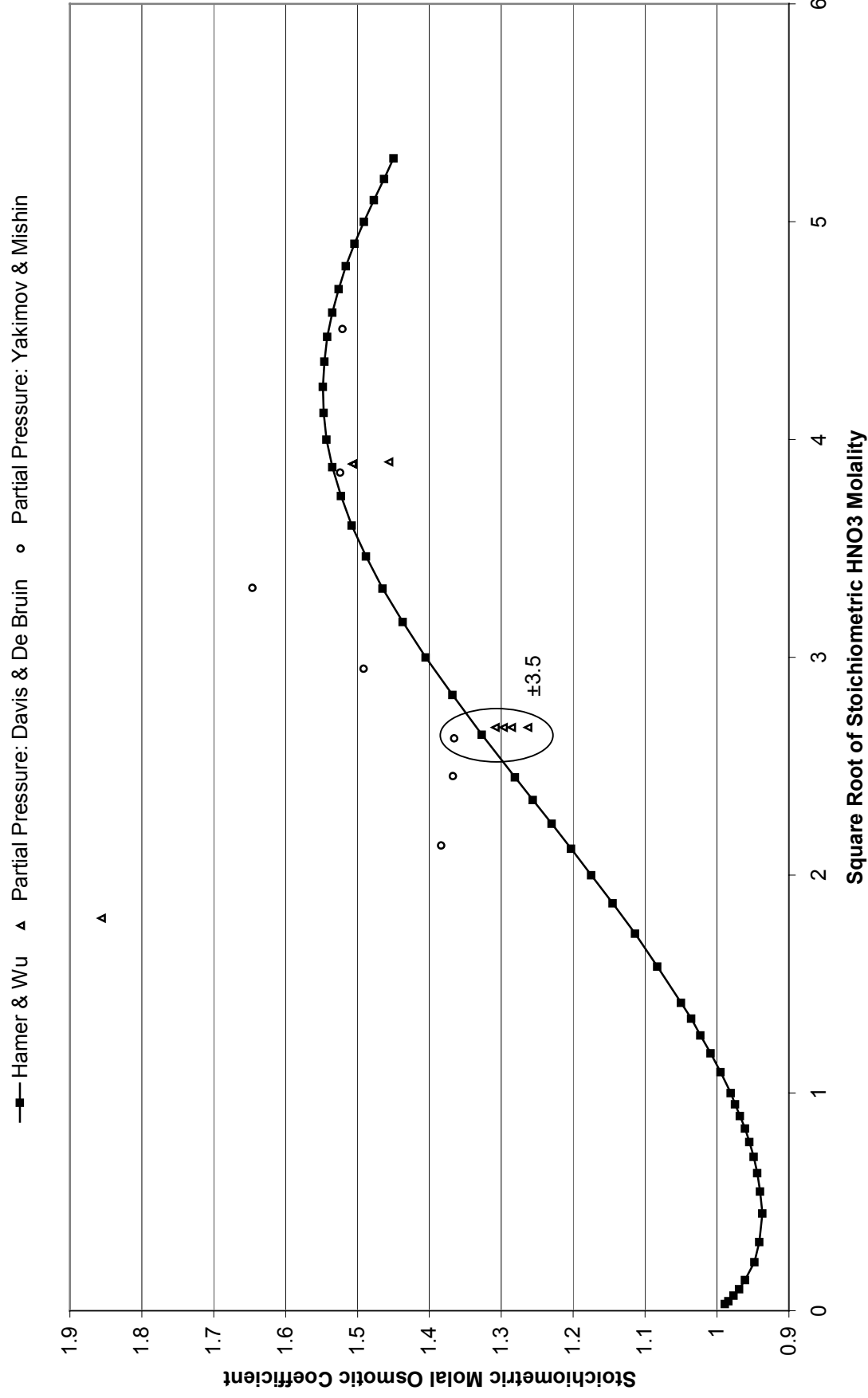


Figure 20. Comparison of Osmotic Coefficients Calculated From VLE Data:  $\text{HNO}_3\text{-H}_2\text{O}$  System @  $20^\circ\text{C}$ .

### Osmotic Coefficient From H2O Partial Pressure: $\text{HNO}_3\text{-H}_2\text{O}$ @ $20^\circ\text{C}$

△ Sproesser & Taylor      □ Potier

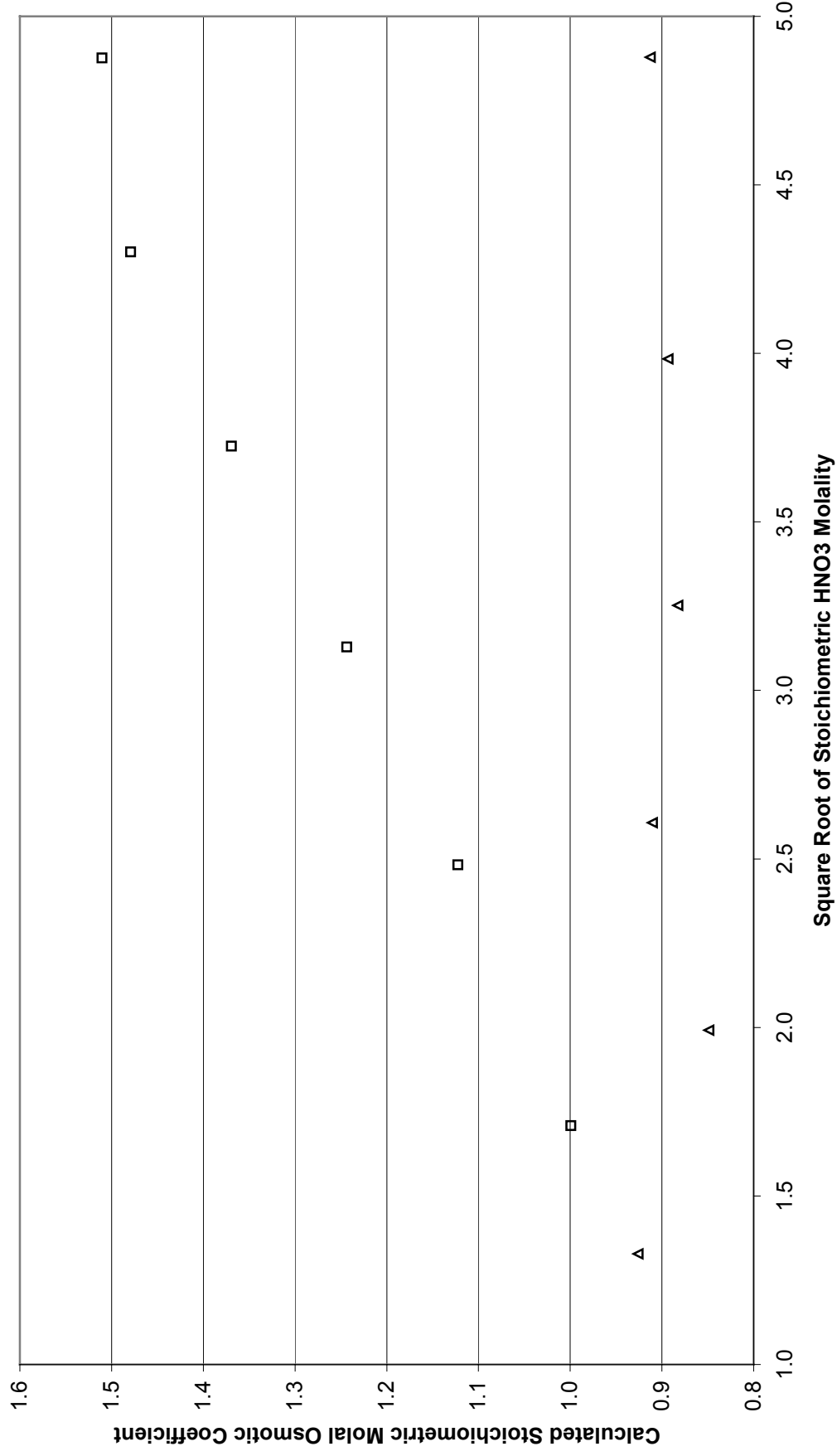


Figure 21. Comparison Of  $\text{HNO}_3$  Partial Pressure Data Used By Clegg & Brimblecombe (1990):  $\text{HNO}_3\text{-H}_2\text{O}$  System @25° C.

### $\text{HNO}_3$ Partial Pressure @ 25 C

○ Burdick & Freed      □ Davis & De Bruin      △ Tang et al.      \* Yakimov & Mishin

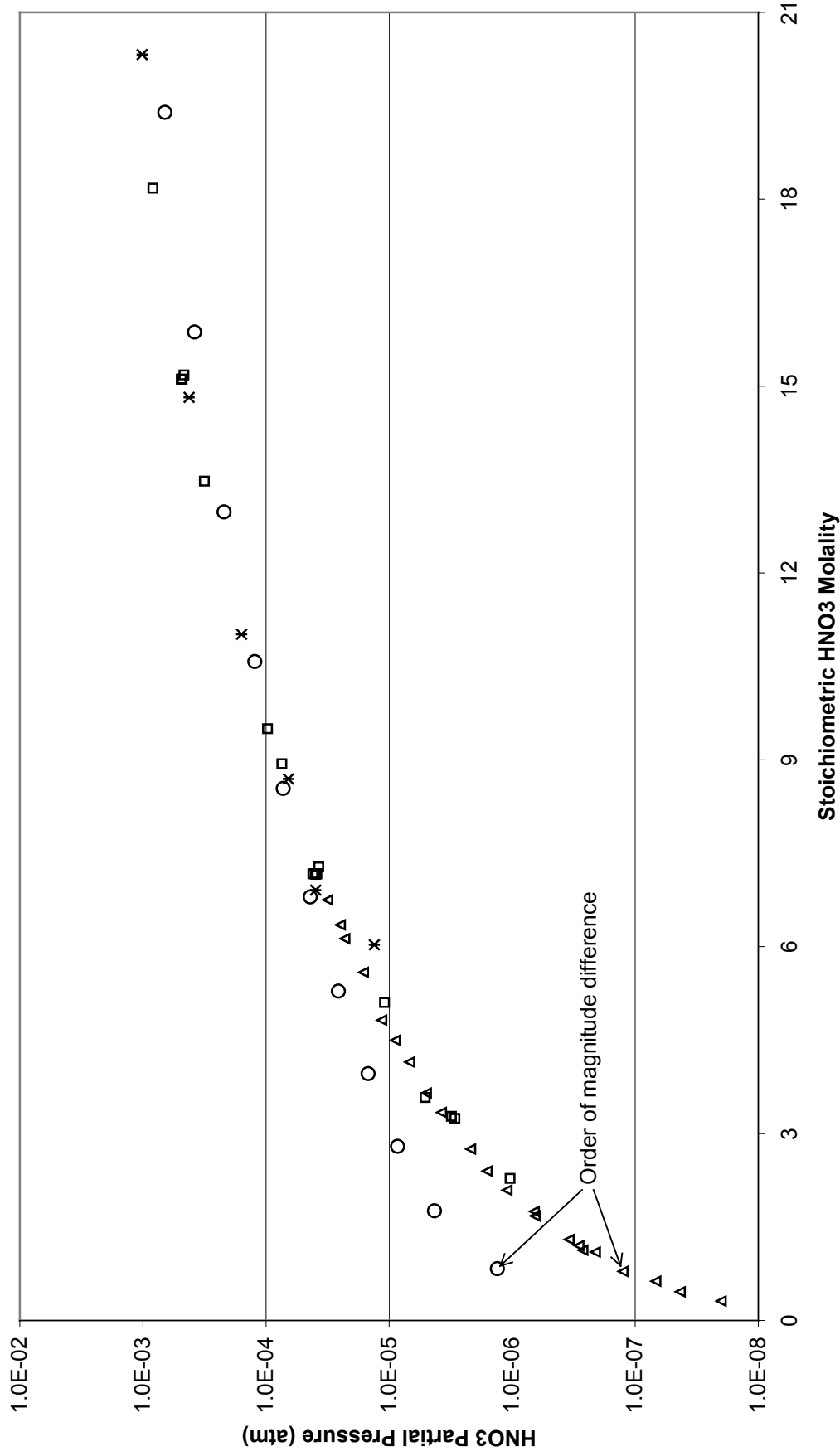


Figure 22. Comparison Of  $\text{HNO}_3$  Partial Pressure Data Used By Clegg & Brimblecombe (1990):  $\text{HNO}_3\text{-H}_2\text{O}$  System @50° C.

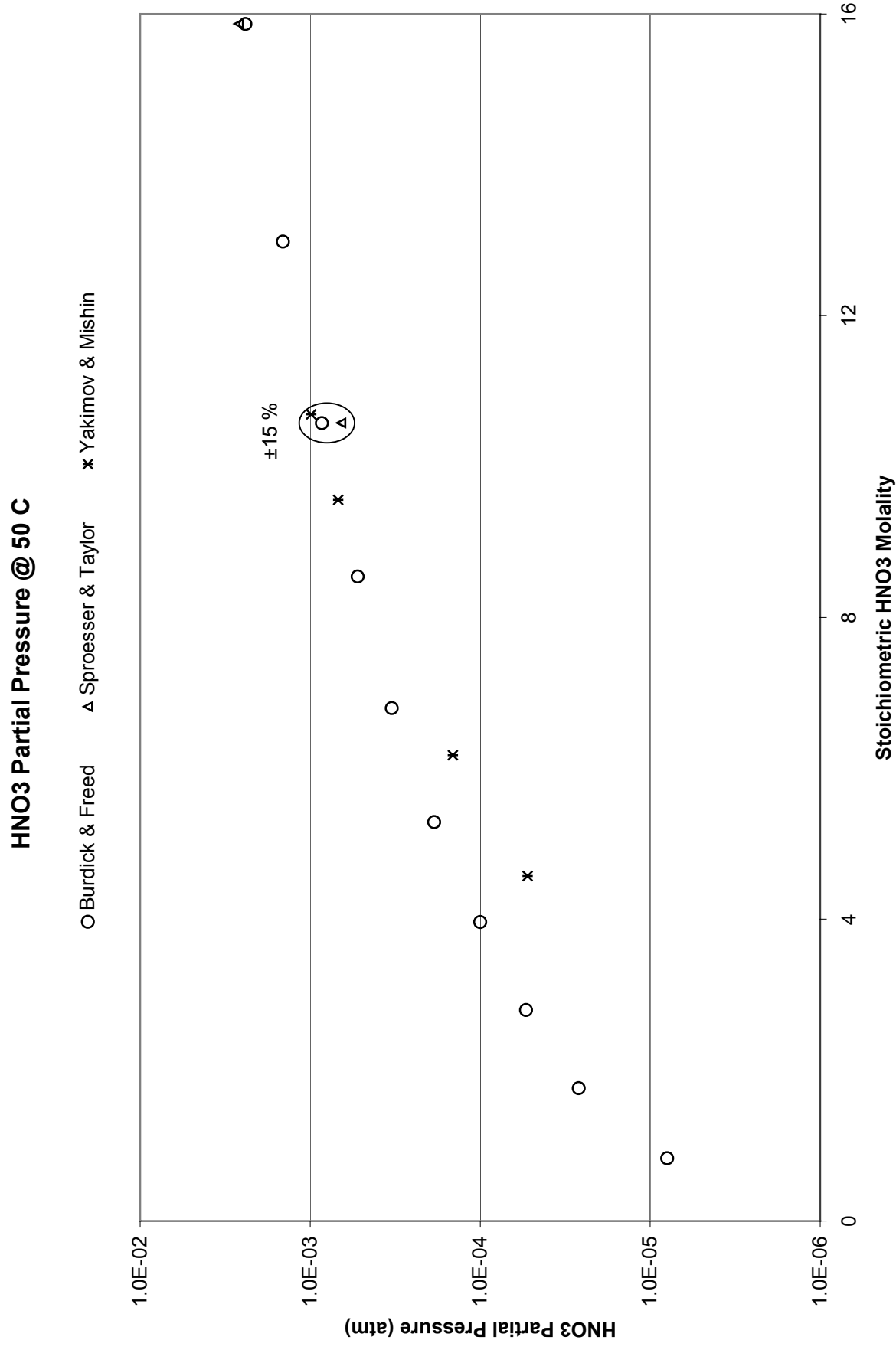


Figure 23. Nitric Acid Dissociation @25° C.

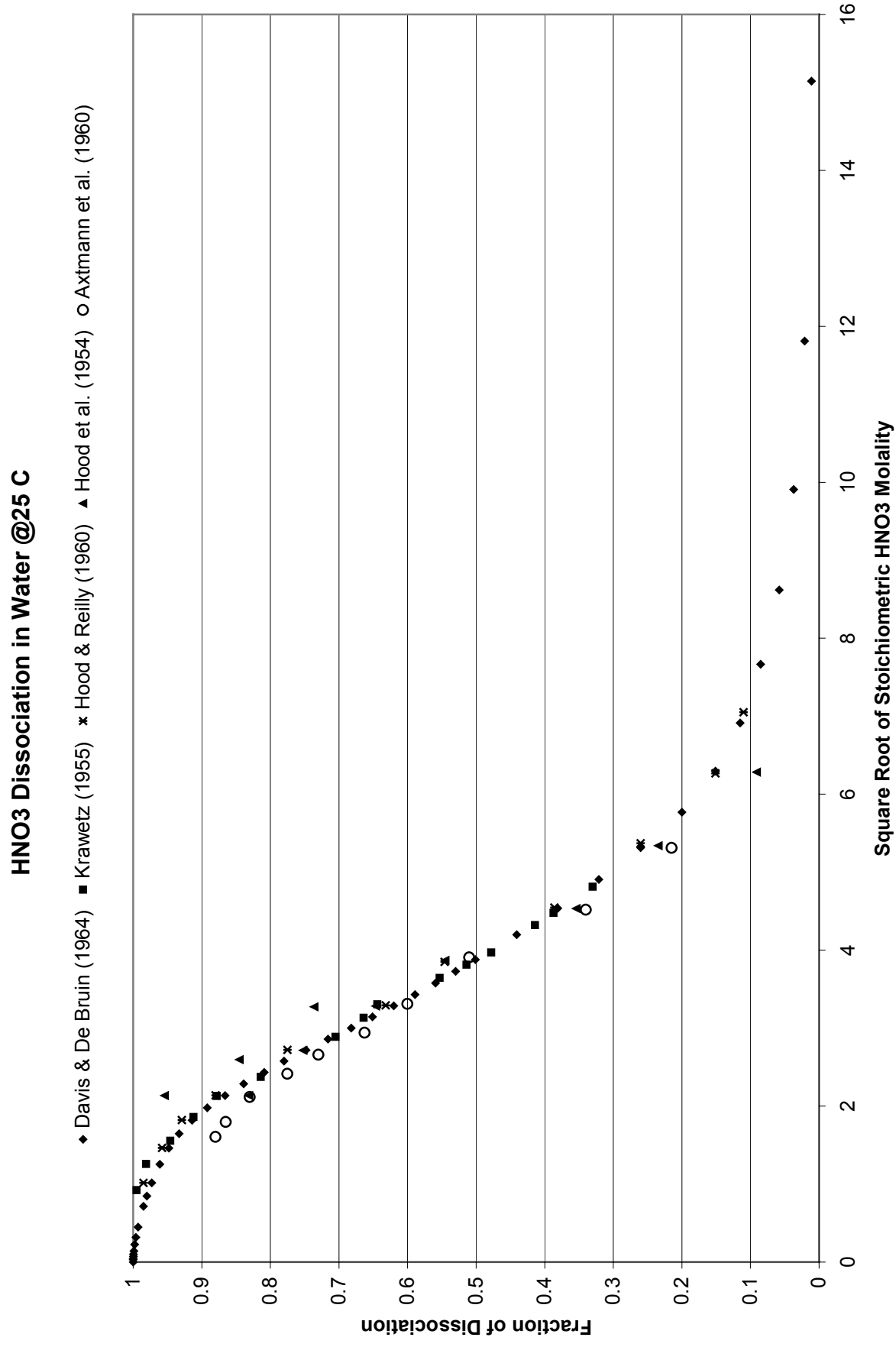


Figure 24. Multi-temperature Dissociation Data of Axtmann et al. (1960):  $\text{HNO}_3\text{-H}_2\text{O}$  System.

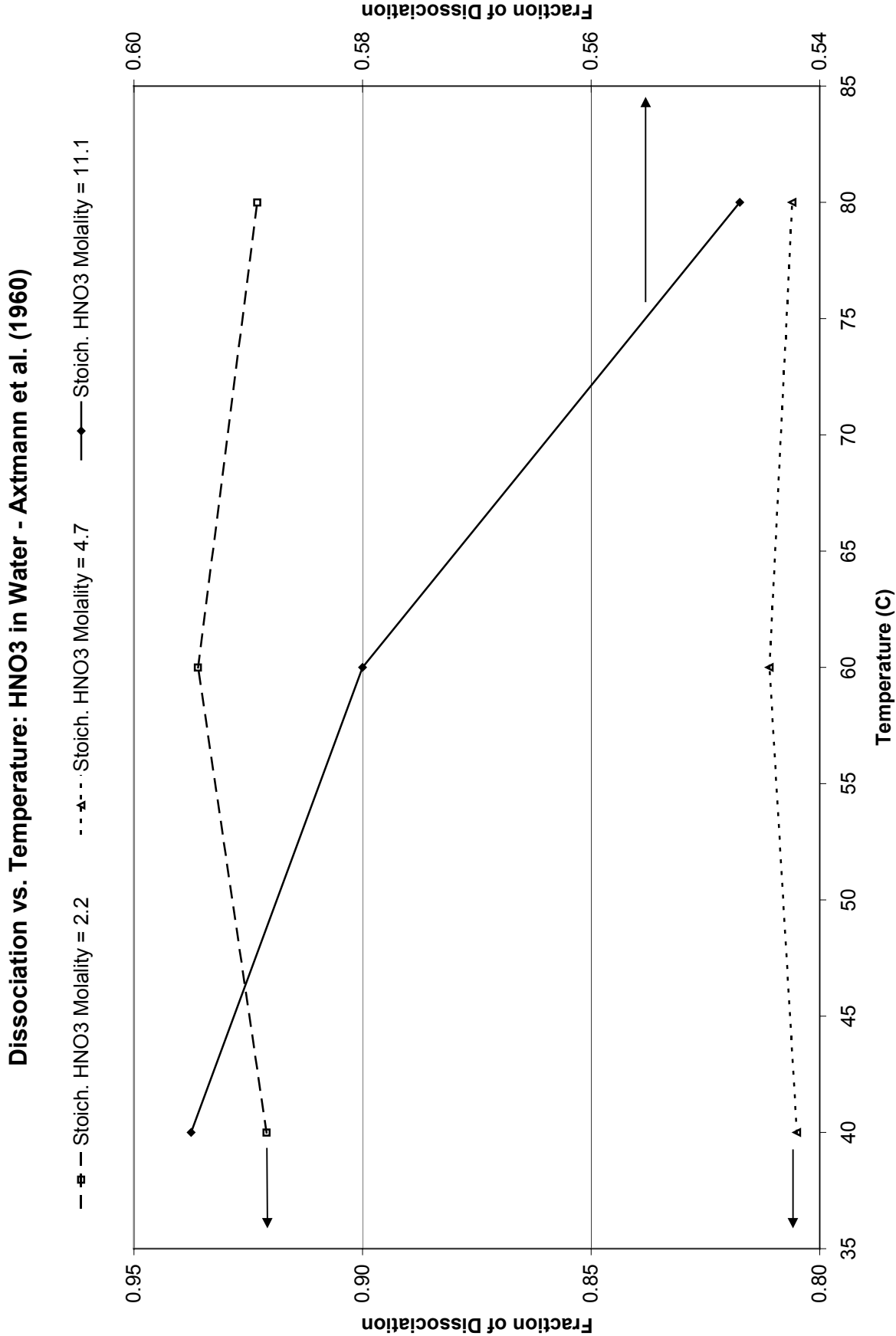


Figure 25. Comparison of  $\text{HNO}_3$  Activity Coefficient Data @25° C.

### $\text{HNO}_3$ Stoichiometric Molal Activity Coefficient In Aqueous Solution @25 C

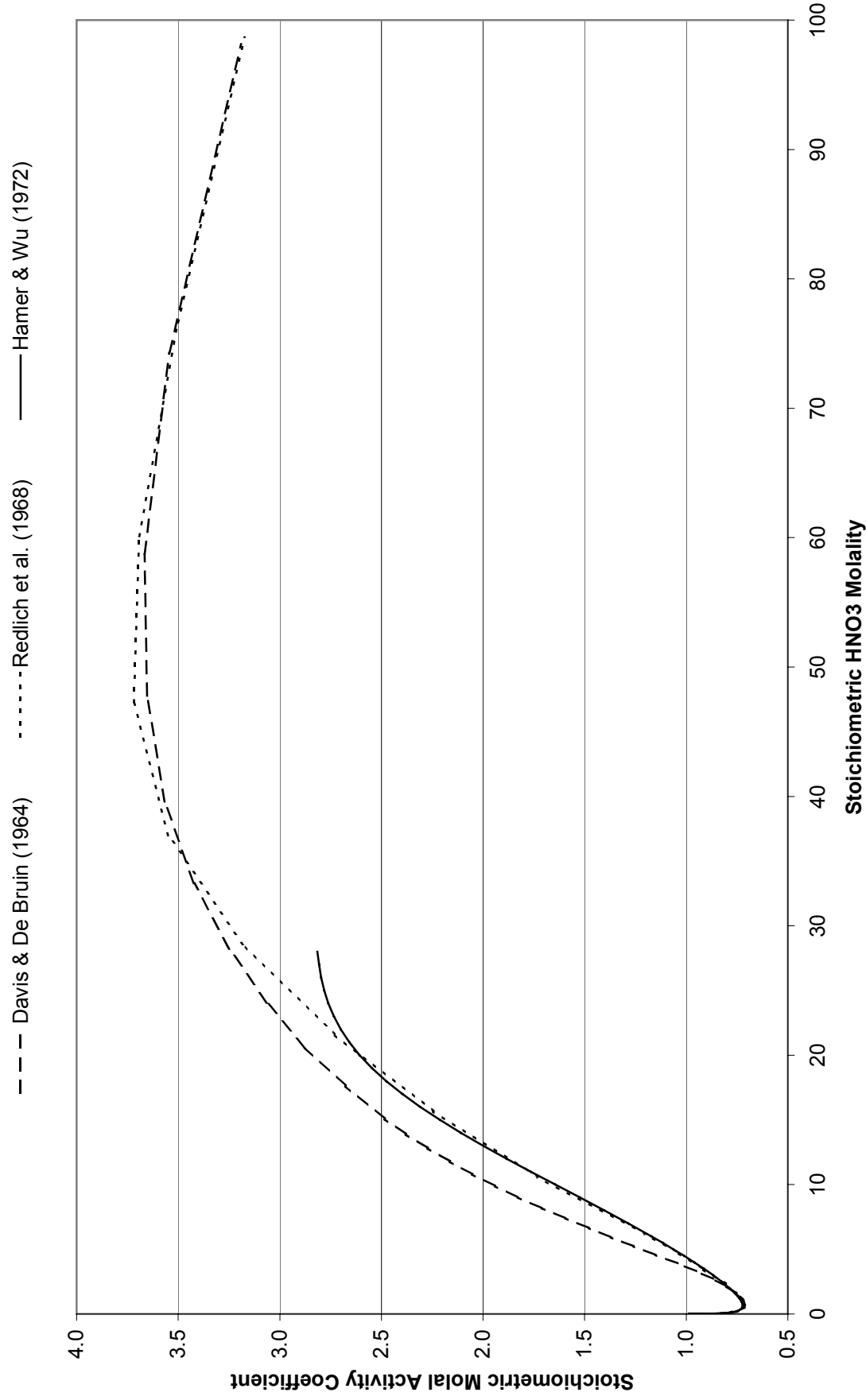




Figure 26. Isothermal Fit of  $\beta_{(H^+,NO_3^-)}^0$ .

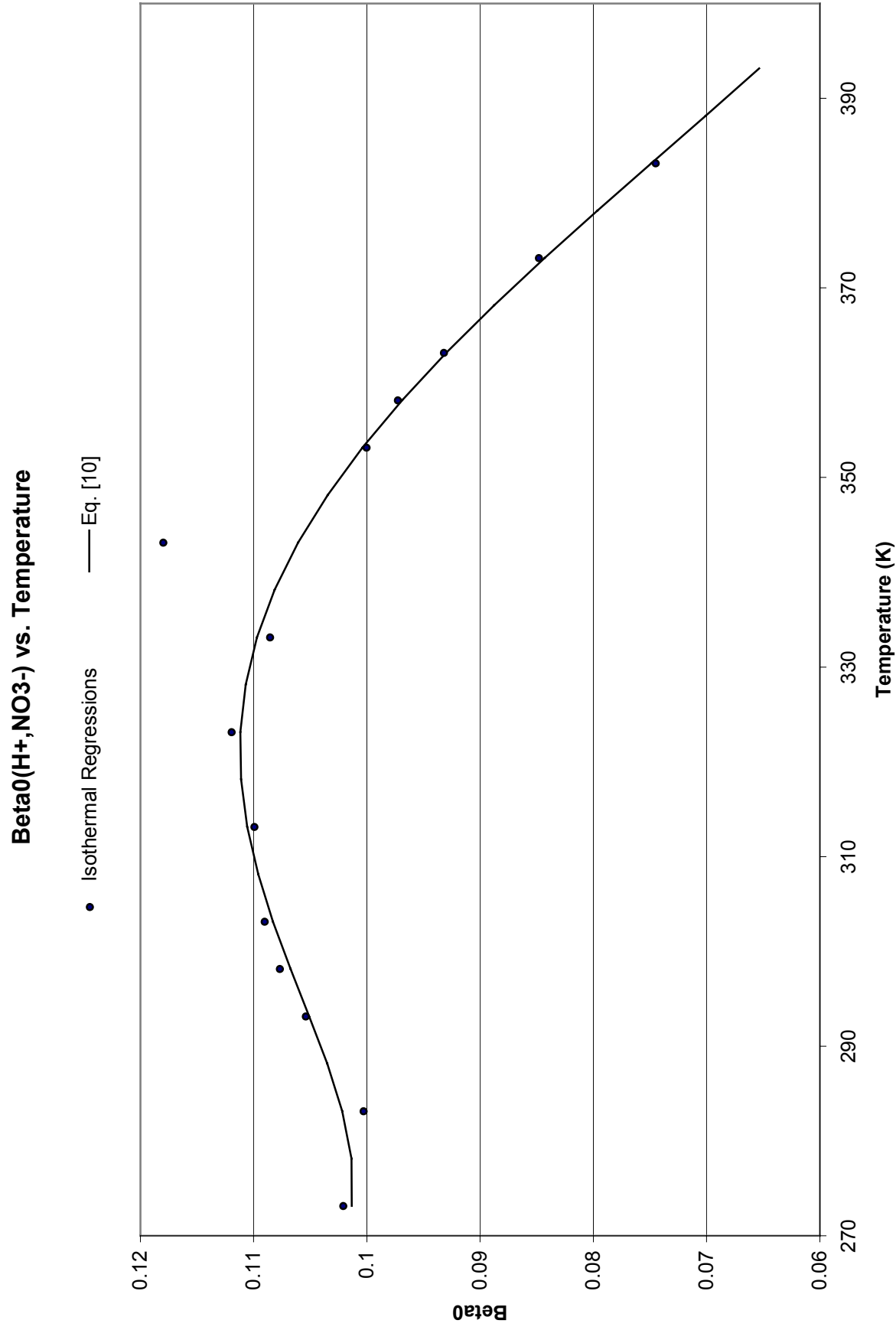


Figure 27. Isothermal Fit of  $\psi_{(HNO_3, HNO_3, HNO_3)}$  ·

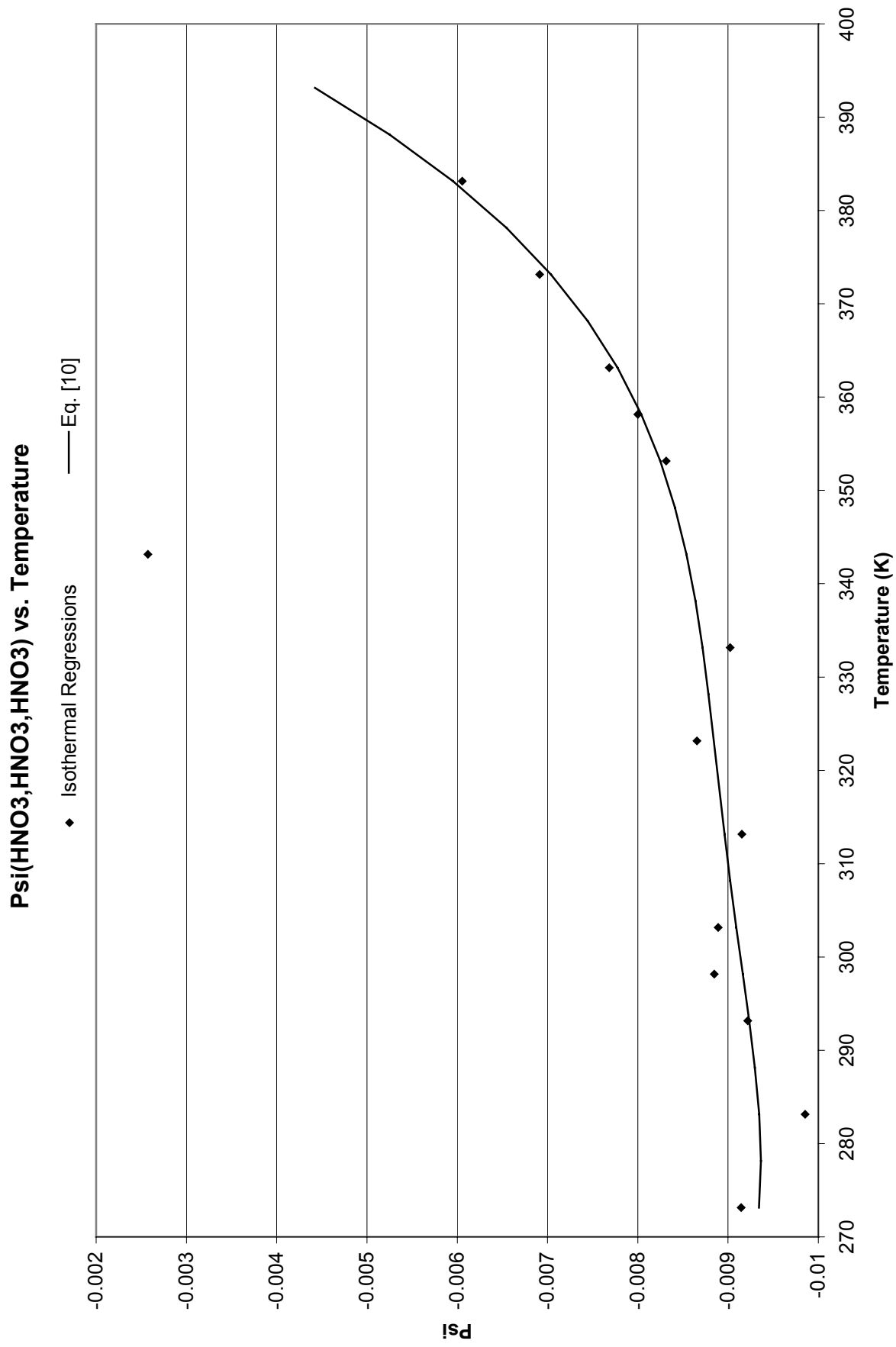


Figure 28. Multi-temperature Extent of Dissociation of Aqueous Nitric Acid: Model vs. Data @0, 25, and 70° C.

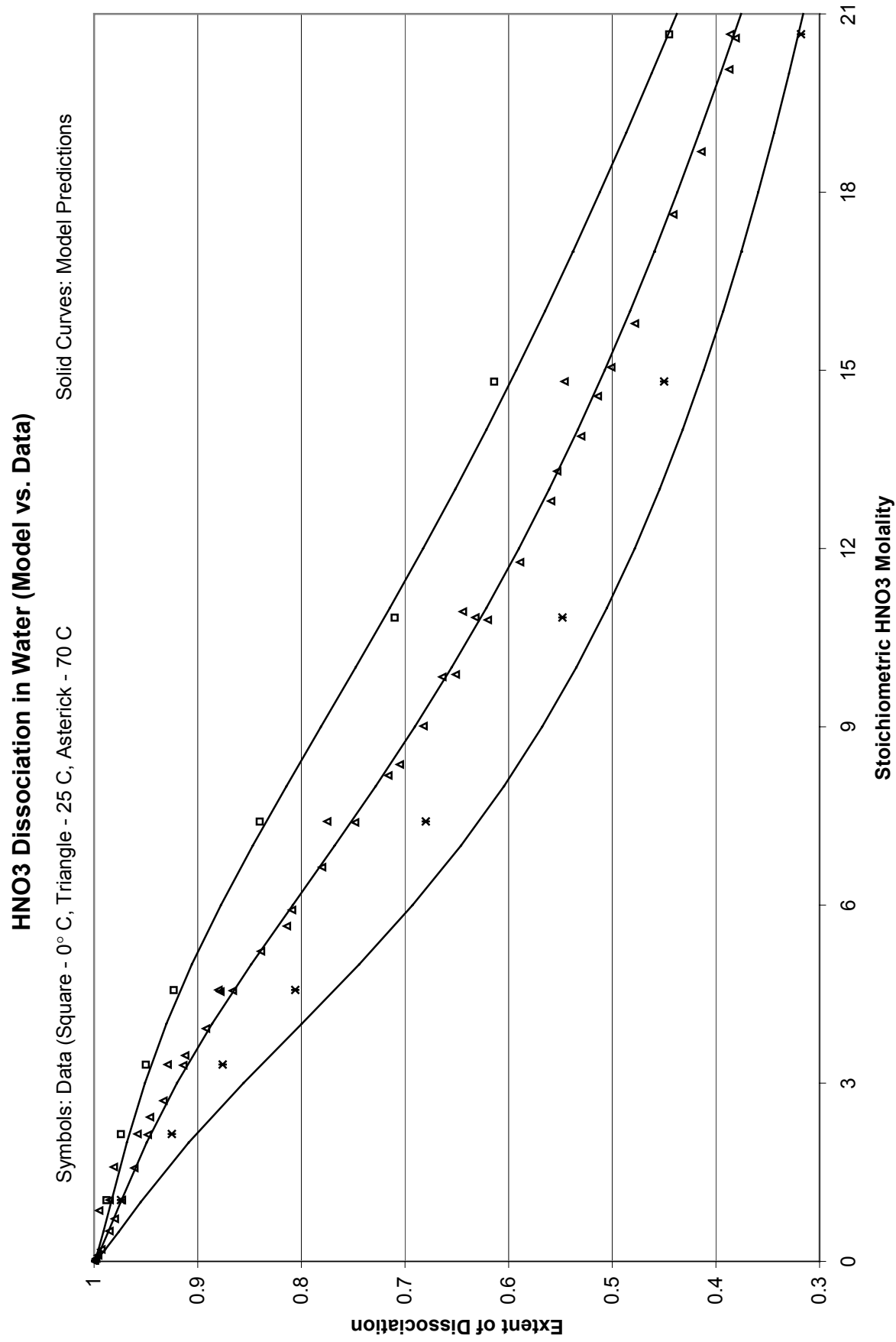


Figure 29. Multi-temperature Extent of Dissociation of Aqueous Nitric Acid: Model vs. Unregressed Data of Krawetz at 0 & 50° C.

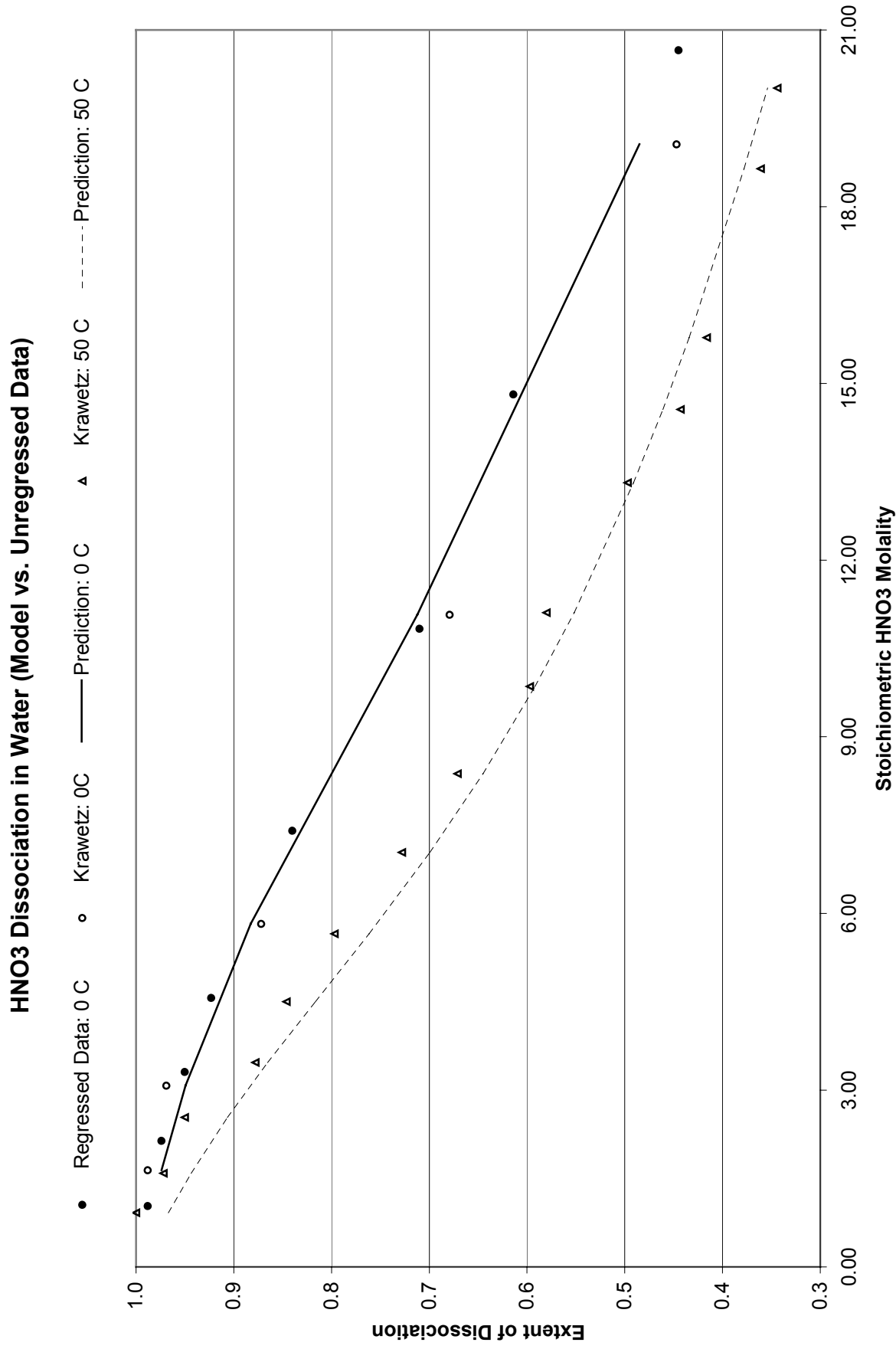


Figure 30. Multi-temperature Predictions of  $\text{HNO}_3$  Dissociation in Water.

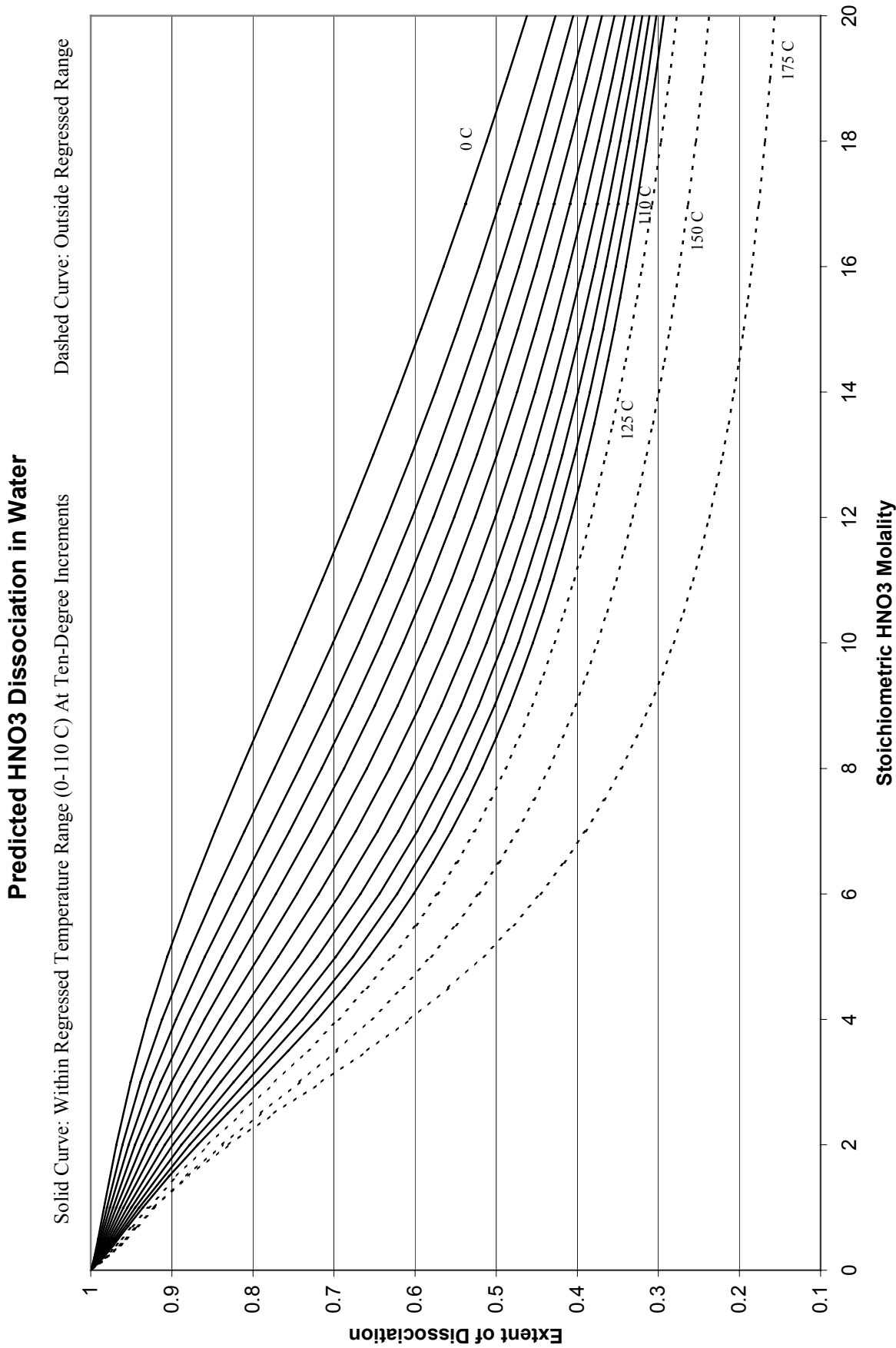


Figure 31. Multi-temperature Stoichiometric  $\text{HNO}_3$  Activity Coefficient in Water: Predictions vs. Regressed Input.

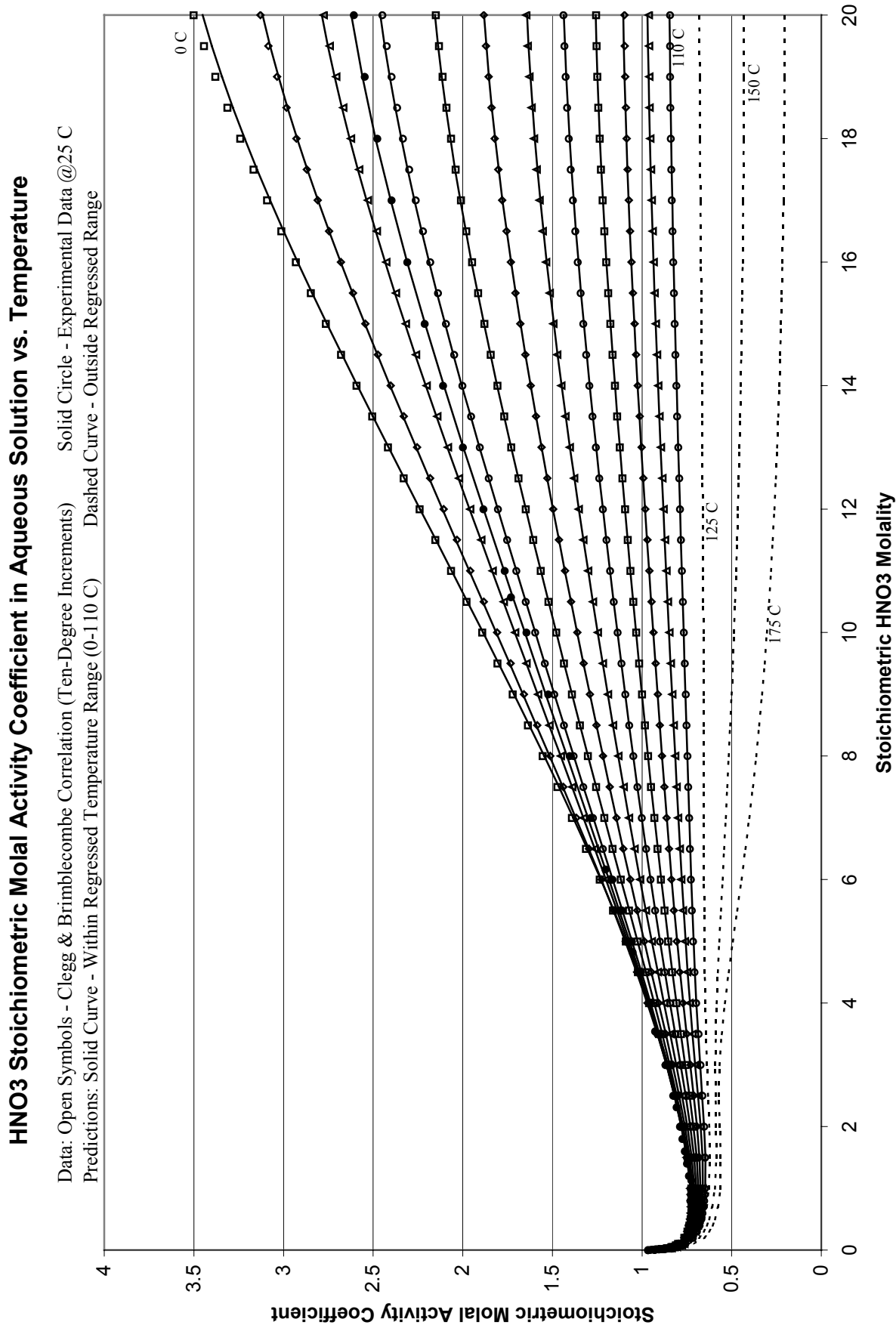


Figure 32. Osmotic Coefficient for Aqueous  $\text{HNO}_3$  @25° C: Model vs. Data.

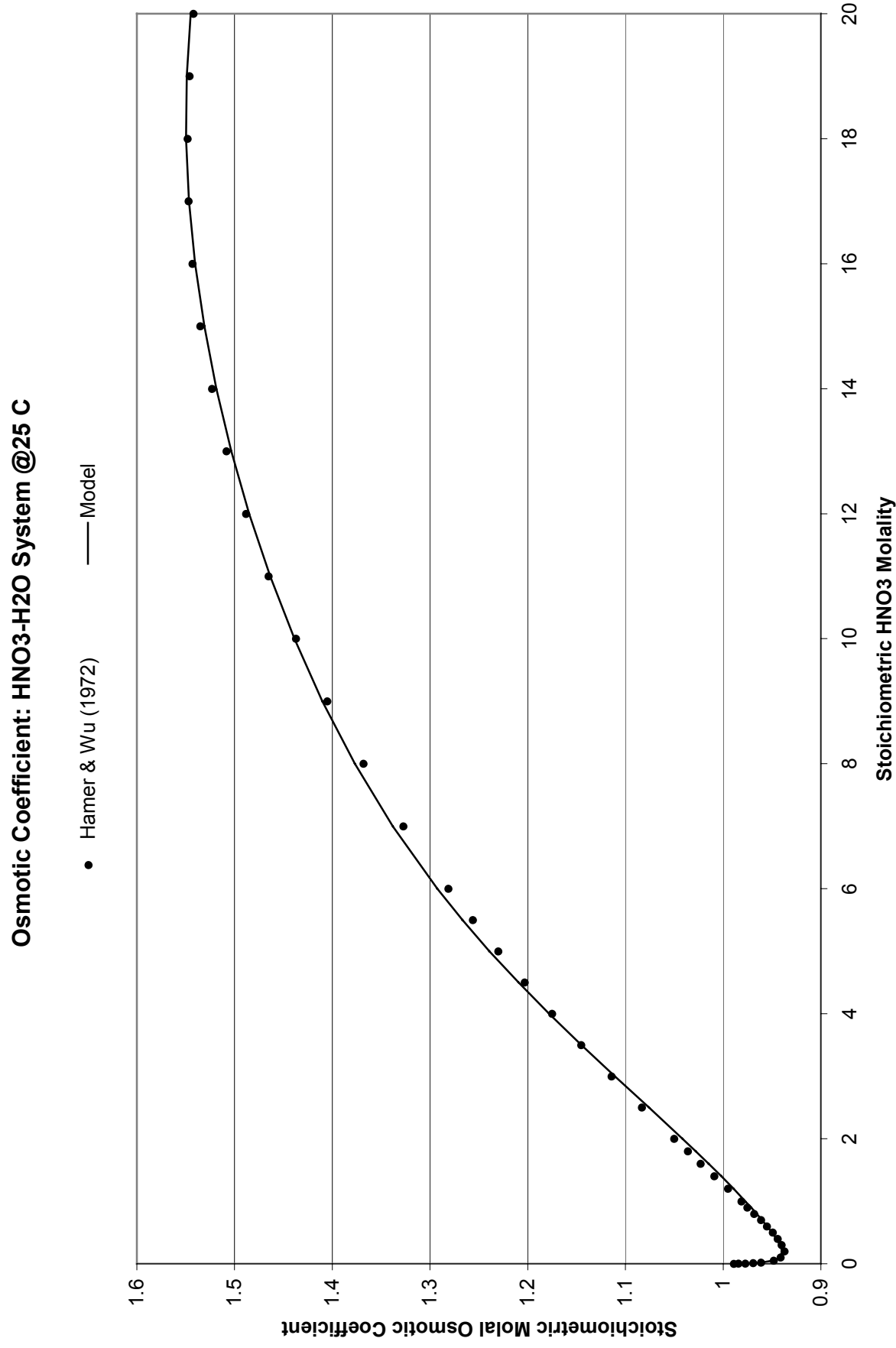


Figure 33. Predicted Osmotic Coefficient for Aqueous  $\text{HNO}_3$  vs. Concentration and Temperature.

### Predicted Stoichiometric Molal Osmotic Coefficient: $\text{HNO}_3\text{-H}_2\text{O}$ System

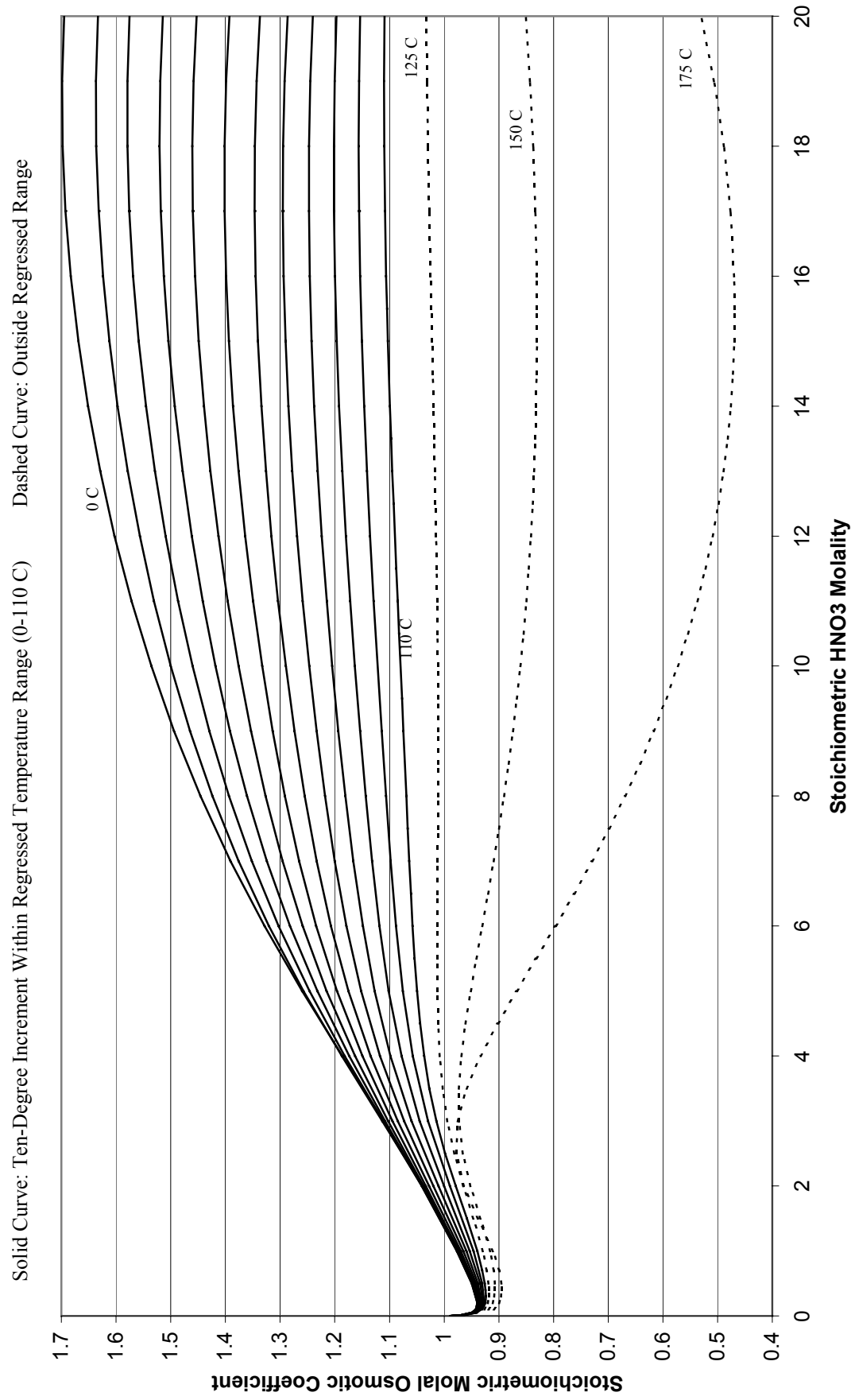




Figure 34. Activity Coefficient of Associated  $\text{HNO}_3$  in Water @25° C.

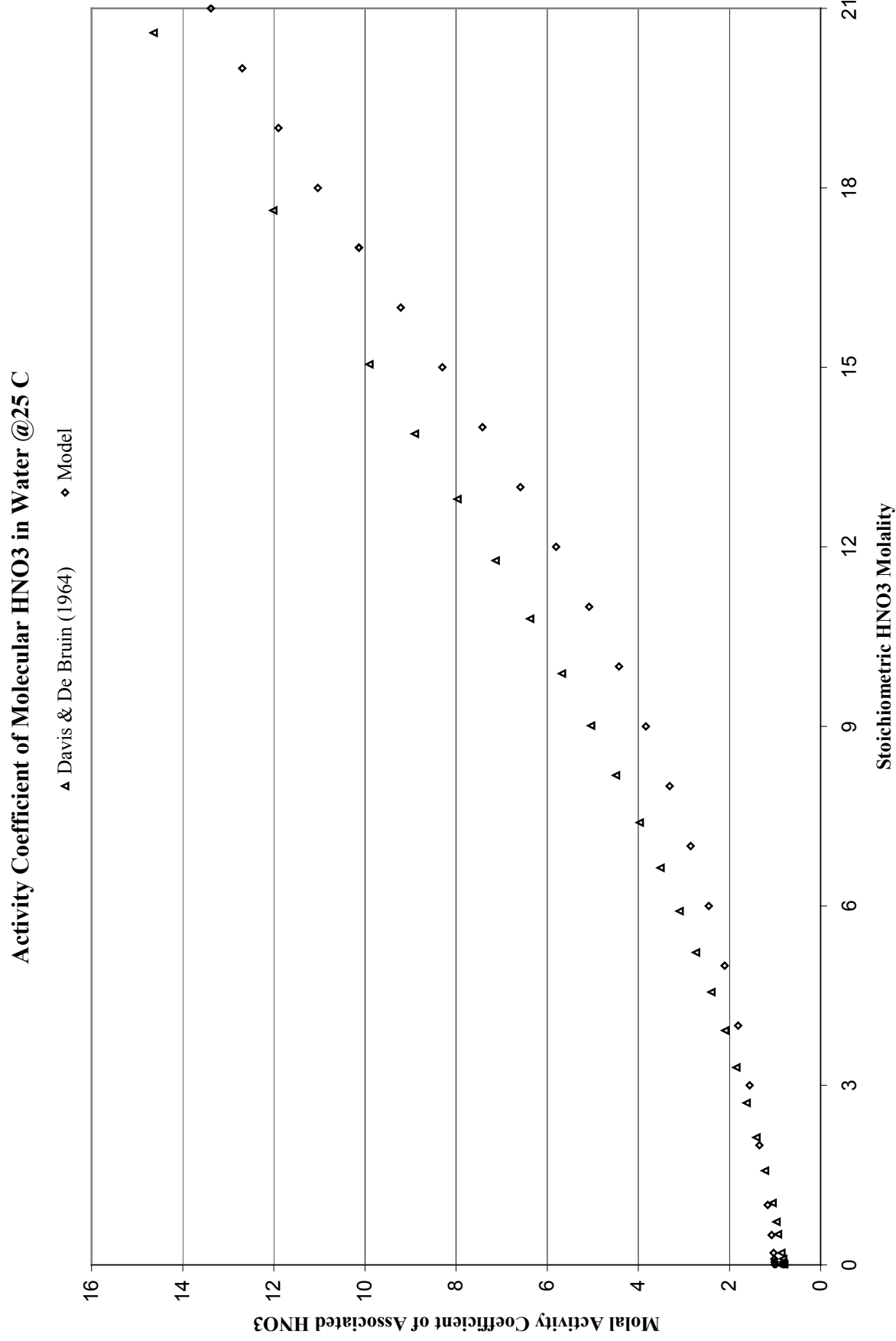


Figure 35. Multi-temperature Predictions of the Activity Coefficient of Associated  $\text{HNO}_3$  in Water.

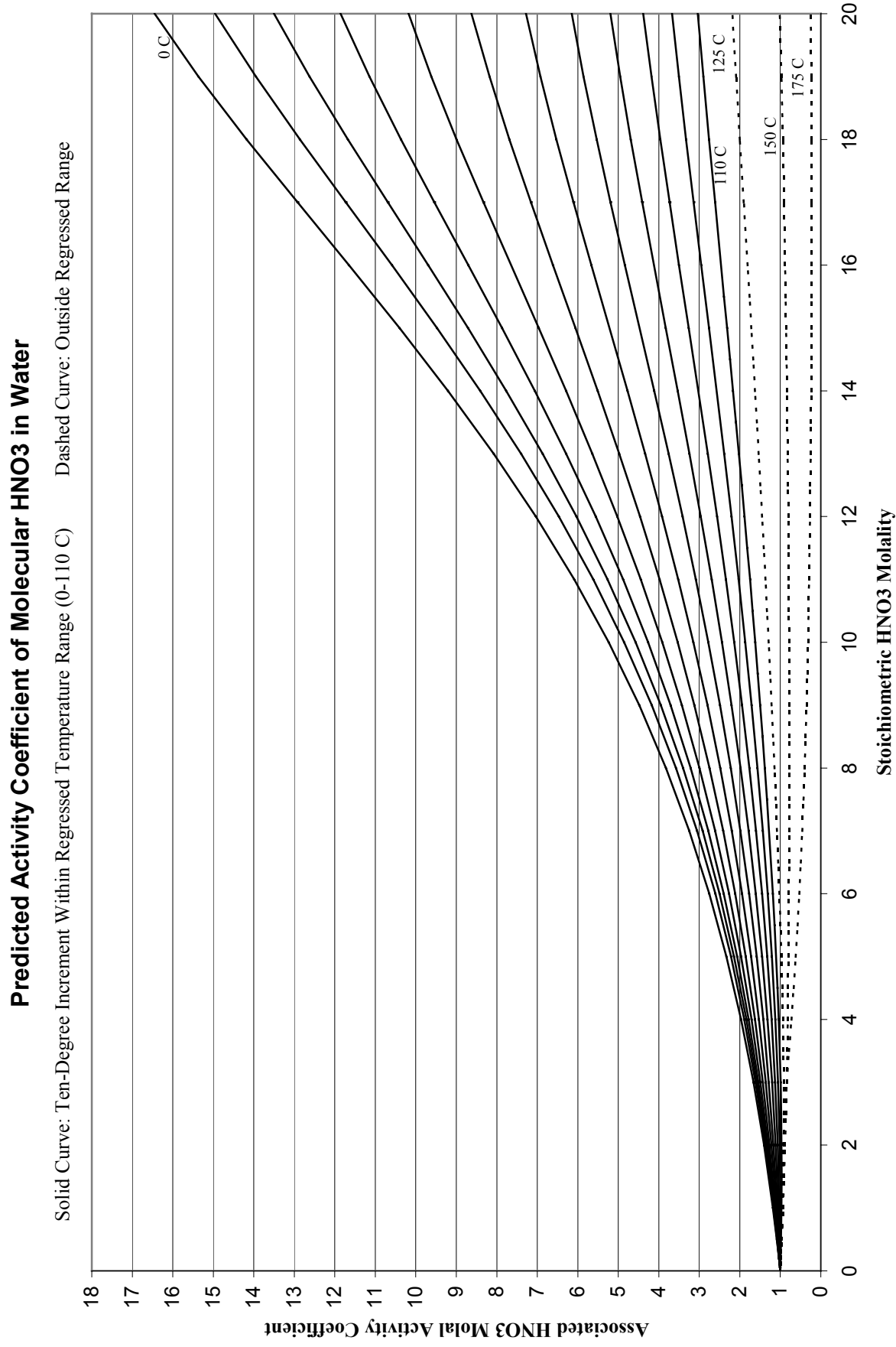


Figure 36. Comparison of HNO<sub>3</sub> Henry's Law Constants in ASPEN Plus Functional Form.

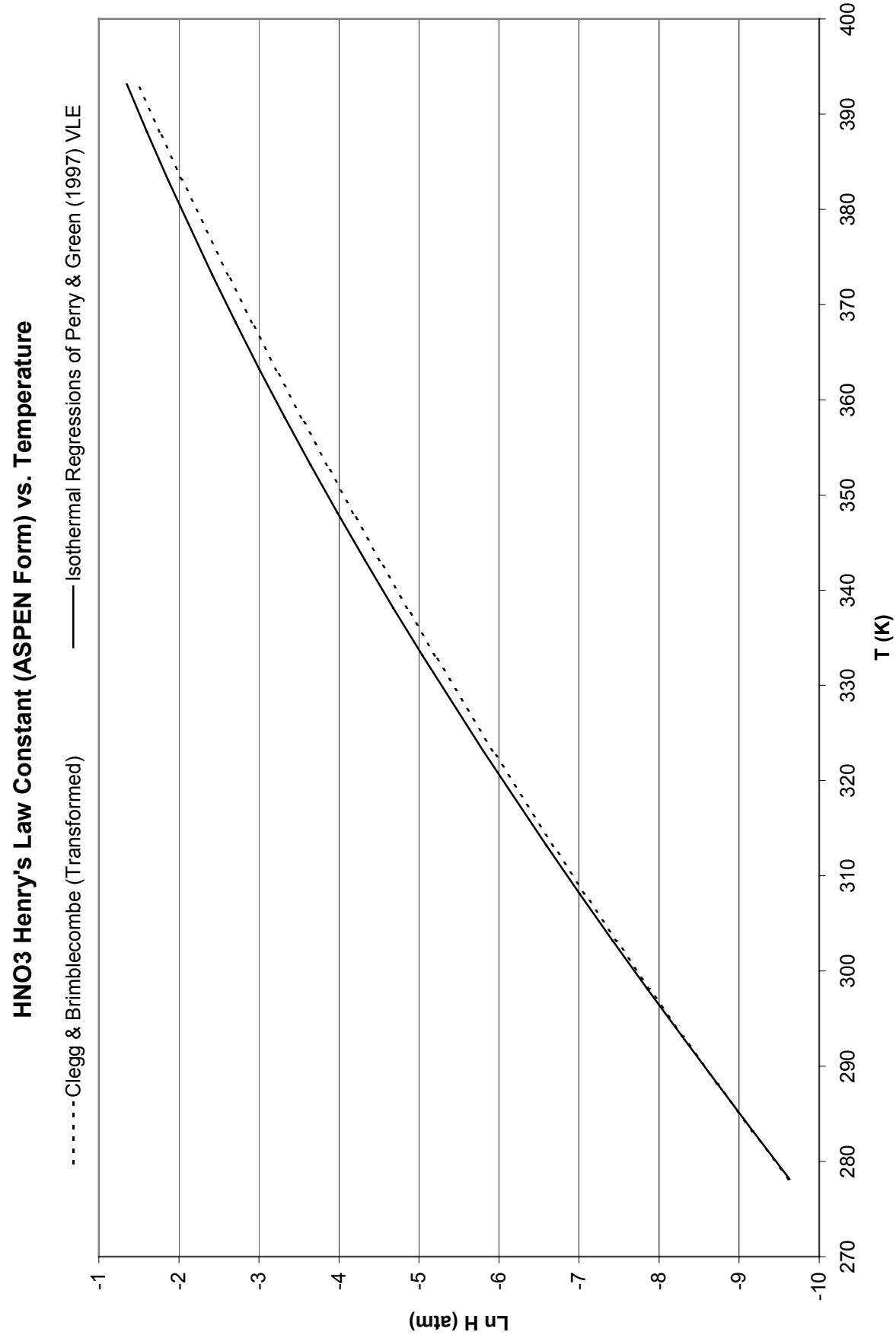


Figure 37. Multi-temperature  $\text{HNO}_3$  Partial Pressure in Aqueous Solution: Predictions vs. Data.

**$\text{HNO}_3$  Partial Pressure vs. Temperature & Concentration:  $\text{HNO}_3\text{-H}_2\text{O}$  System**

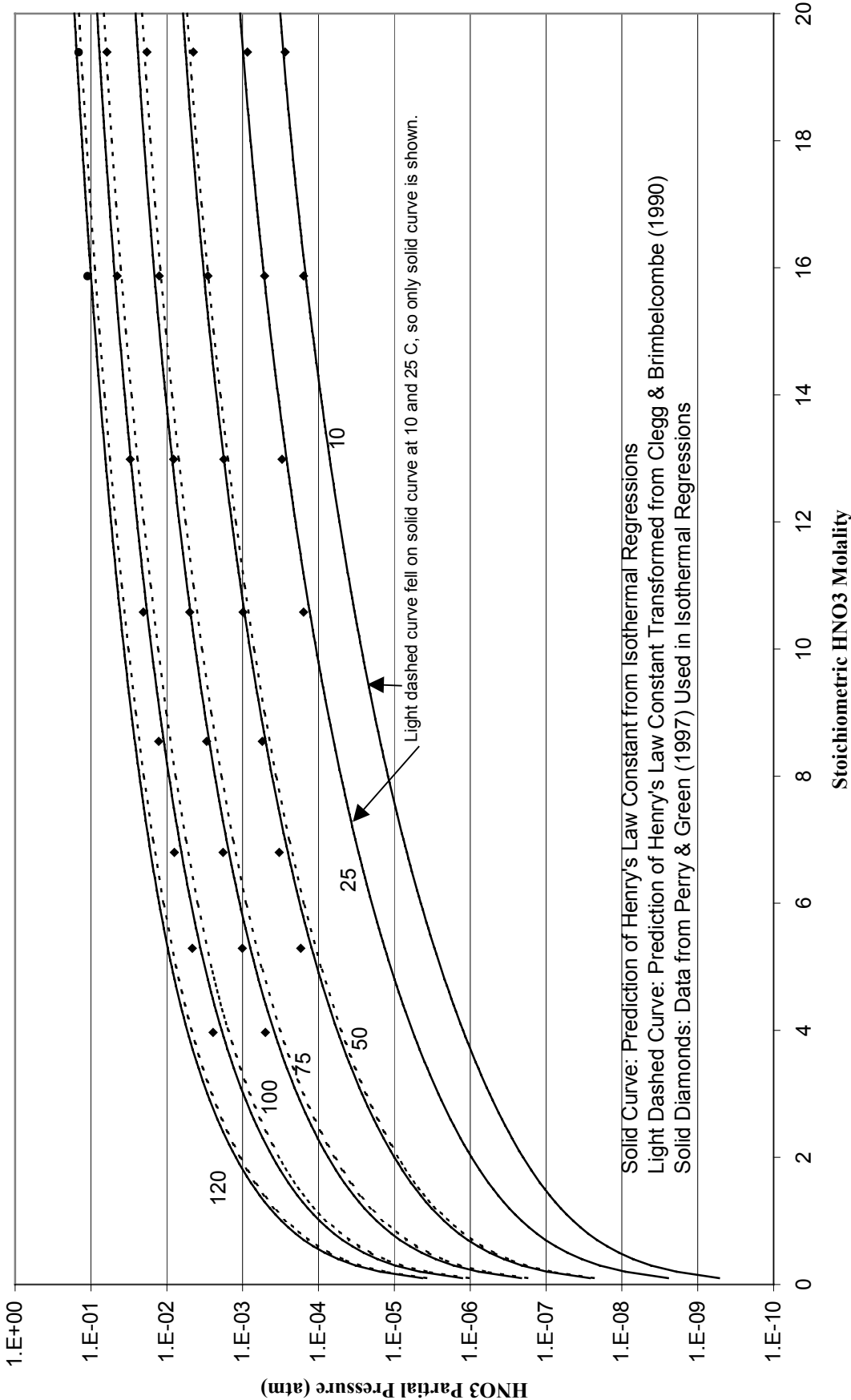


Figure 38. Comparison Of Association-Based And Complete-Dissociation Pitzer Models: HCl @25° C.

### Activity Coefficient of Aqueous HCl at 25 C

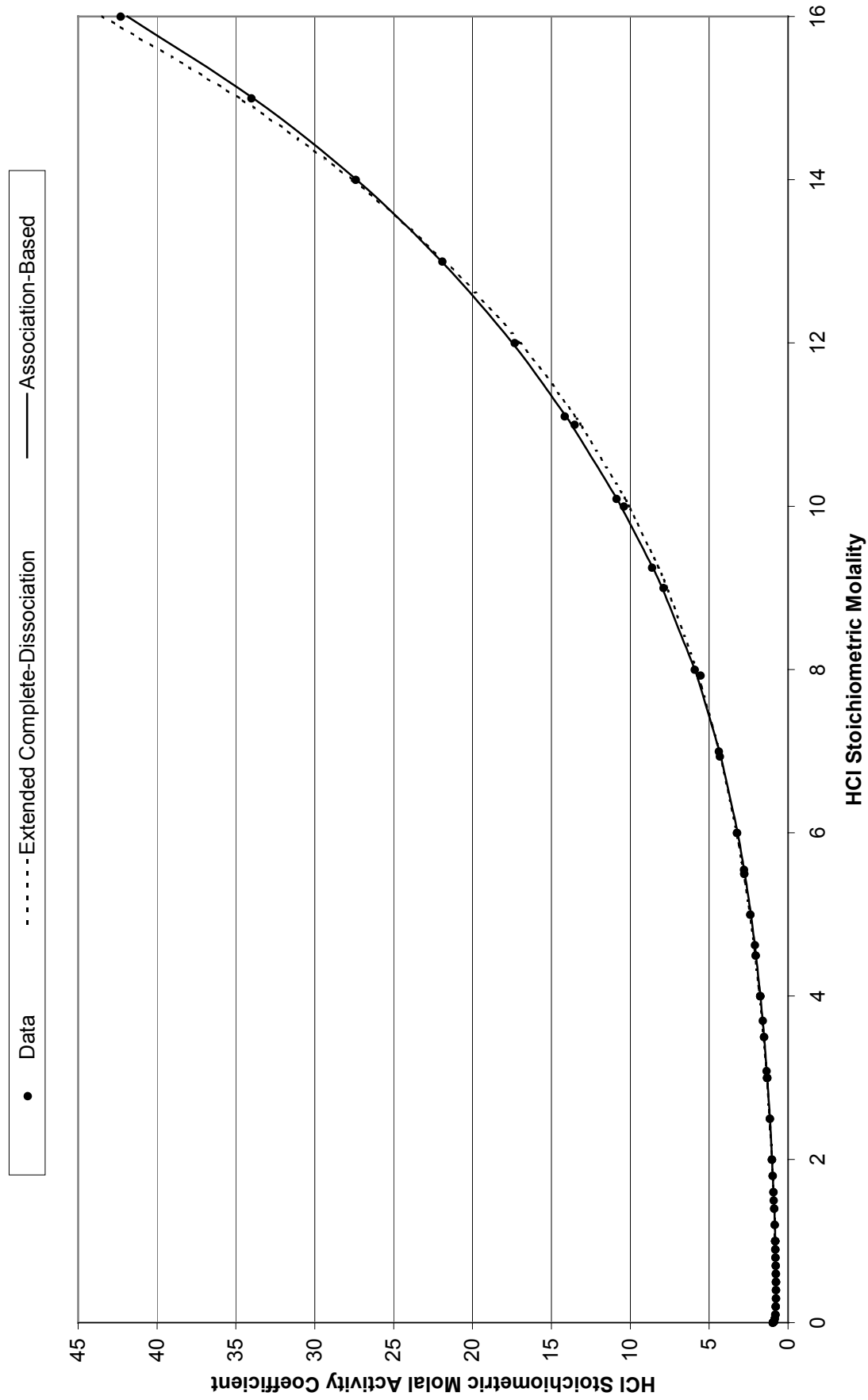


Figure 39. Comparison Of Association-Based And Complete-Dissociation Pitzer Models:  $\text{HNO}_3$  @25° C.

### Activity Coefficient of Aqueous $\text{HNO}_3$ at 25 C

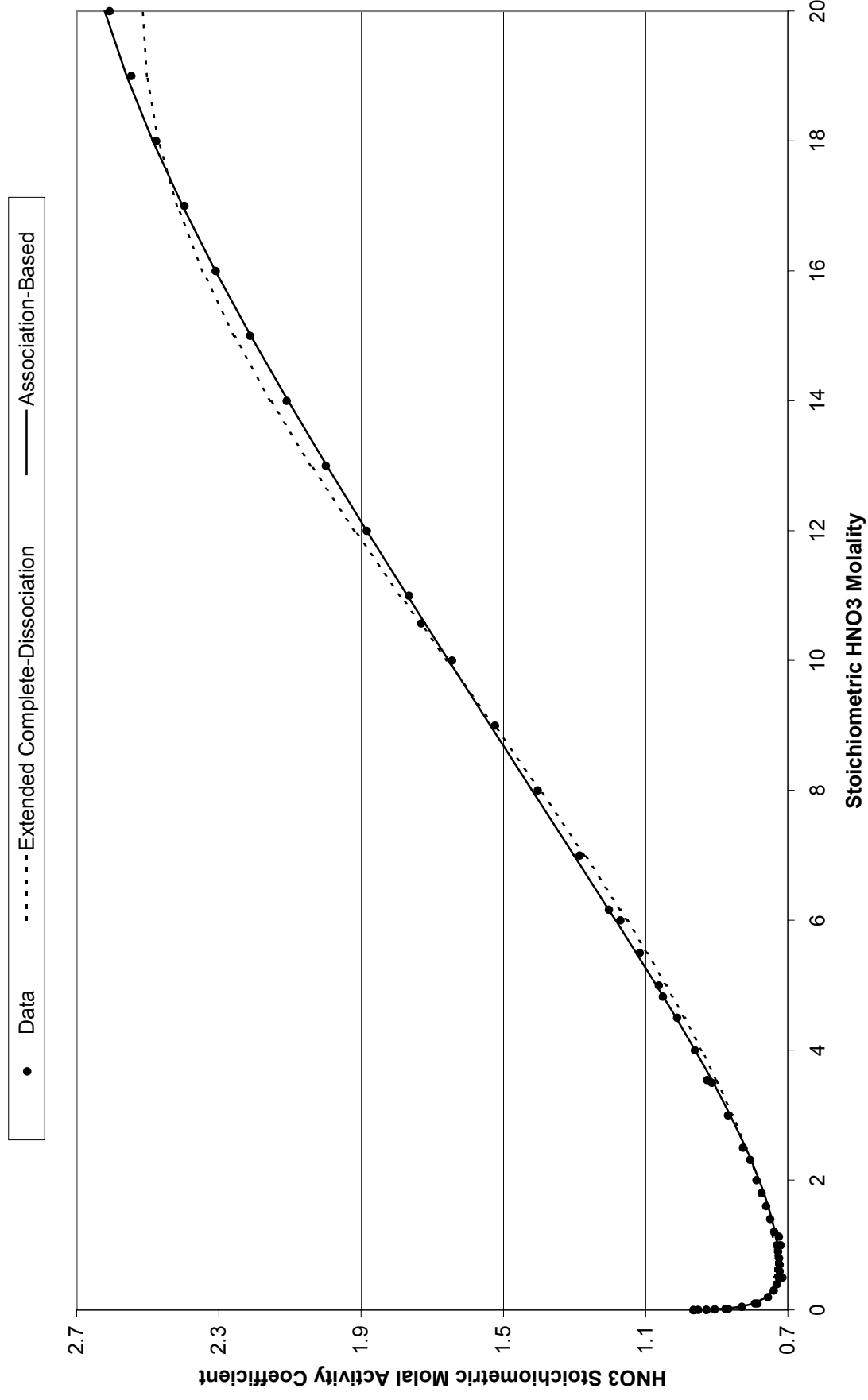


Figure 40. Comparison Of Deviations: Association-Based vs. Extended Complete-Dissociation for HCl @25° C.

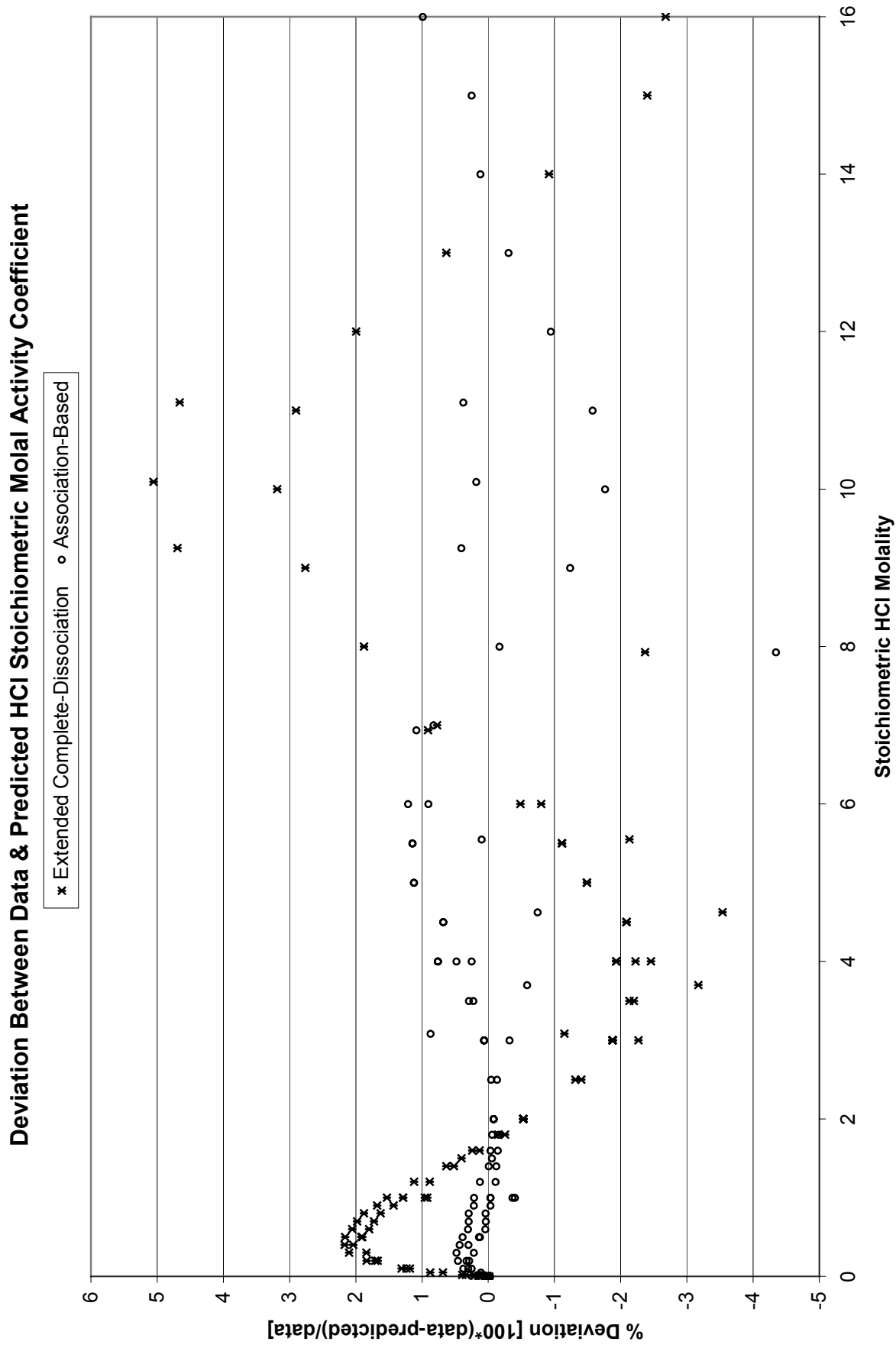


Figure 41. Comparison Of Deviations: Association-Based vs. Extended Complete-Dissociation for  $\text{HNO}_3$  @25° C.

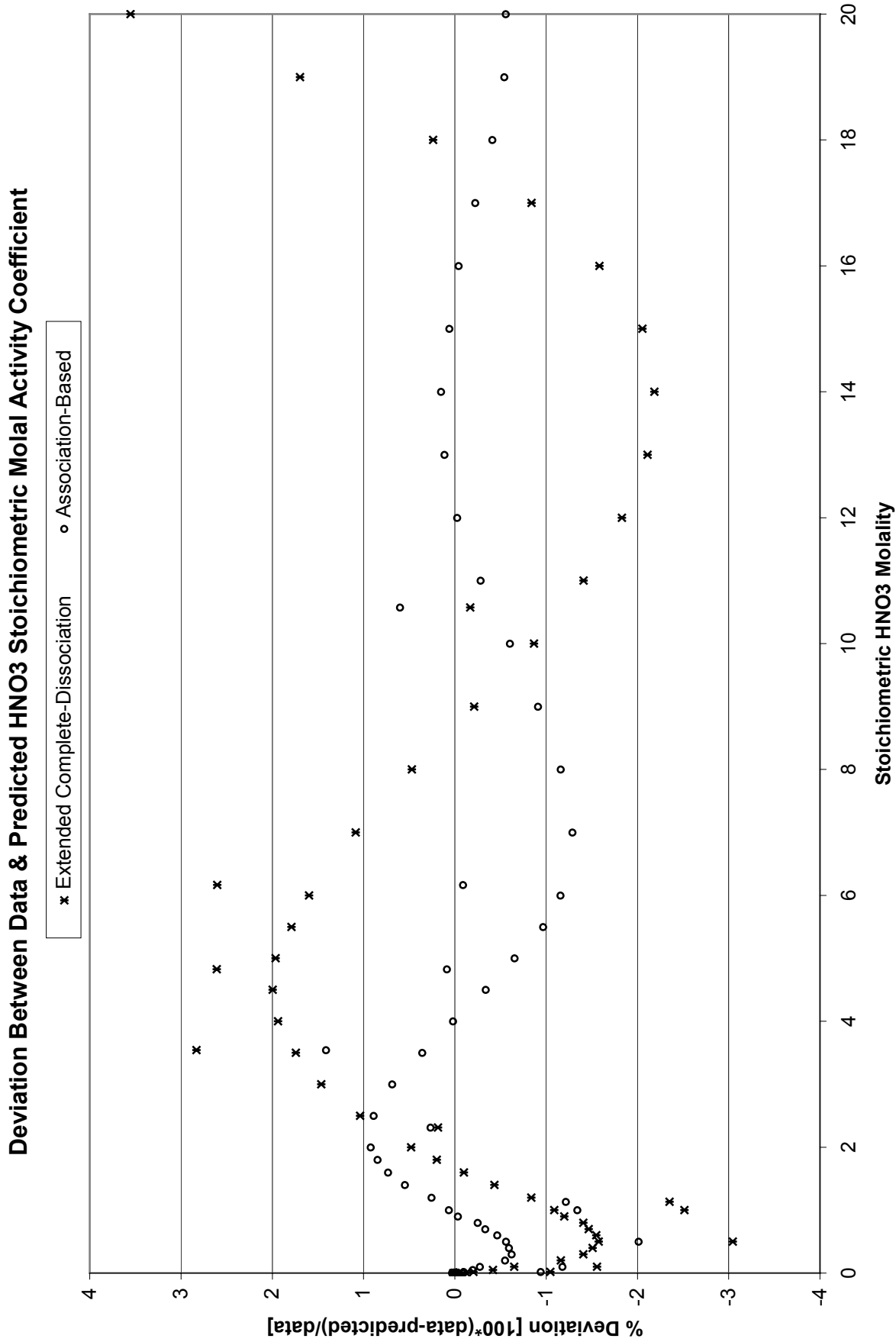




Figure 42. Deviation Of Complete-Dissociation Pitzer (1991) Parameterization For  $\text{HNO}_3$  Data Of Hamer & Wu (1972) @25° C.

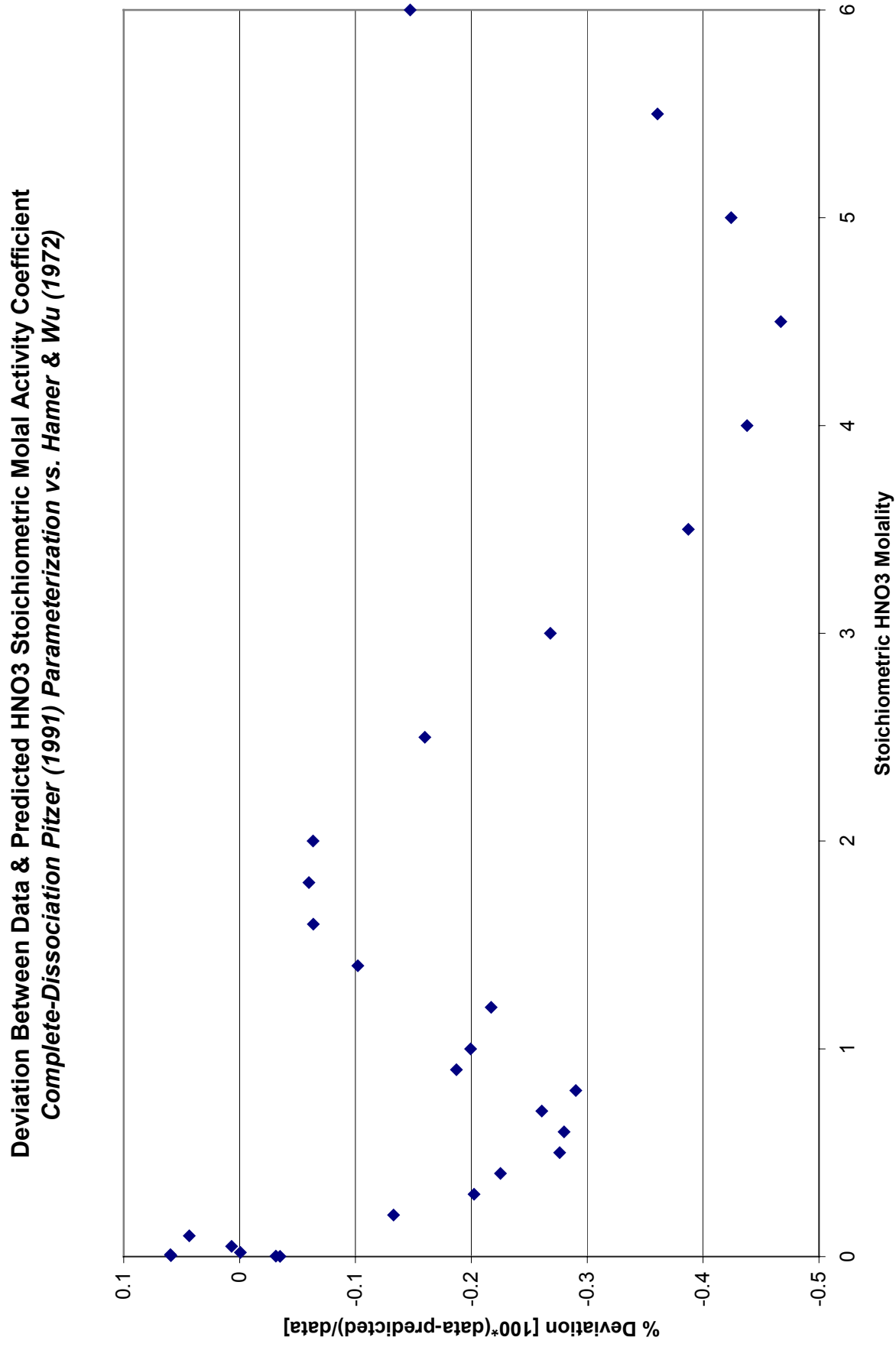


Table 1. HCl Partial Pressure of Aqueous Hydrochloric Acid Solution at Total Pressure of 1 Atm.

Boiling Point T (C)	Stoich. HCl Molality	HCl Partial Pressure (atm)		% Abs. Dev. [100*abs(Data-Pred)/Data]
		Data*	Model	
101.05	1.260261	0.0006	0.000264	55.93
102.35	2.204632	0.0025	0.001143	54.28
104.95	3.827132	0.0088	0.007225	17.90
106.95	8.419252	0.247	0.249411	0.98
107.05	5.282737	0.0321	0.027614	13.97
107.15	8.397173	0.2398	0.248234	3.52
108.15	7.727396	0.1751	0.168785	3.61
108.35	6.546809	0.0806	0.075897	5.84
108.55	6.818552	0.1014	0.092855	8.43
108.55	7.163366	0.1251	0.117835	5.81
Average				17.01

\* From Sako et al. (1984)

Table 2. HCl Partial Pressure of Aqueous Hydrochloric Acid Solution at Total Pressure of 1 Atm.

Boiling Point T(C)	Stoich. HCl Molality	Predicted HCl Partial Pressure (atm)			Predicted Total Pressure (atm)				
		Luckas & Eden	Our Model	% Abs. Dev.	Our Model	Data*	Luckas & Eden	% Deviation	
								Our Model	Luckas & Eden
50.25	1.262	5.54E-06	5.66E-06	2.06	0.117582	0.119023	0.117582	1.21	1.21
50.35	10.042	0.030974	0.032179	3.89	0.086207	0.086553	0.085002	0.40	1.79
50.35	13.435	0.24072	0.23321	3.12	0.268839	0.272588	0.276349	1.38	-1.38
50.65	6.644	0.00232	0.002434	4.91	0.08322	0.085369	0.083106	2.52	2.65
50.95	8.567	0.010976	0.011713	6.72	0.078007	0.079941	0.07727	2.42	3.34
71.35	1.262	3.09E-05	3.15E-05	2.07	0.311877	0.311374	0.311877	-0.16	-0.16
73.25	13.435	0.733245	0.77053	5.09	0.8814	0.867506	0.844114	-1.60	2.70
77.75	10.042	0.162142	0.160015	1.31	0.358016	0.349766	0.360143	-2.36	-2.97
78.65	6.644	0.015811	0.015703	0.68	0.308586	0.311276	0.308694	0.86	0.83
78.65	8.567	0.065094	0.064569	0.81	0.305996	0.309993	0.30652	1.29	1.12
86.75	13.435	1.317937	1.463596	11.05	1.663493	1.566741	1.517833	-6.18	3.12
91.45	1.262	0.000139	0.000138	0.96	0.697666	0.695781	0.697667	-0.27	-0.27
91.45	6.644	0.035936	0.033208	7.59	0.522236	0.523069	0.524964	0.16	-0.36
100.05	10.042	0.542314	0.483509	10.84	0.970133	0.953368	1.028938	-1.76	-7.93
101.05	8.567	0.242655	0.207505	14.49	0.794652	0.801678	0.829802	0.88	-3.51
101.85	6.644	0.068358	0.058326	14.68	0.781397	0.782235	0.791429	0.11	-1.18
103.75	1.262	0.000331	0.000317	4.33	1.092067	1.087886	1.092082	-0.38	-0.39
112.45	10.042	0.994128	0.824215	17.09	1.590132	1.571281	1.760045	-1.20	-12.01
114.35	1.262	0.000678	0.000623	8.11	1.561988	1.555095	1.562043	-0.44	-0.45
118.95	8.567	0.631345	0.461064	26.97	1.565654	1.600099	1.735935	2.15	-8.49
121.35	6.644	0.214123	0.150891	29.53	1.564152	1.577992	1.627385	0.88	-3.13

\* From Sako et al. (1985)

Table 3. Activity Coefficient of HCl: HCl-KCl-H<sub>2</sub>O System @25° C.

Source	Stoichiometric Molality			$\gamma_{\pm, \text{st (HCl)}}$		
	HCl	KCl	Ionic Strength	Data	Calc	% Abs. Dev.
Harned&Owen	0.010	0.010	0.020	0.874	0.874	0.03
Harned&Owen	0.010	0.020	0.030	0.852	0.853	0.14
Harned&Owen	0.010	0.030	0.040	0.837	0.838	0.07
Harned&Owen	0.010	0.050	0.060	0.816	0.815	0.18
Hawkins	0.010	0.090	0.100	0.778	0.785	0.87
Macaskill&Bates	0.010	0.090	0.100	0.783	0.785	0.24
Harned&Owen	0.010	0.100	0.110	0.782	0.779	0.35
Harned&Owen	0.010	0.200	0.210	0.747	0.744	0.37
Harned&Owen	0.010	0.500	0.510	0.706	0.713	1.00
Hawkins	0.010	0.990	1.000	0.712	0.720	1.15
Harned&Owen	0.010	1.000	1.010	0.720	0.721	0.09
Harned&Owen	0.010	1.500	1.510	0.743	0.751	1.02
Harned&Owen	0.010	2.000	2.010	0.781	0.791	1.28
Hawkins	0.010	2.990	3.000	0.859	0.888	3.38
Harned&Owen	0.010	3.000	3.010	0.860	0.889	3.38
Harned&Owen	0.010	3.500	3.510	0.899	0.944	4.98
Macaskill&Bates	0.030	0.070	0.100	0.786	0.787	0.14
Macaskill&Bates	0.038	0.343	0.381	0.717	0.722	0.79
Hawkins	0.050	0.050	0.100	0.782	0.789	0.88
Macaskill&Bates	0.050	0.050	0.100	0.789	0.789	0.02
Macaskill&Bates	0.067	0.606	0.673	0.705	0.716	1.48
Macaskill&Bates	0.070	0.030	0.100	0.792	0.791	0.08
Macaskill&Bates	0.087	0.785	0.872	0.708	0.721	1.94
Macaskill&Bates	0.090	0.010	0.100	0.794	0.793	0.18
Hawkins	0.100	0.900	1.000	0.712	0.727	2.15
Hawkins	0.100	2.900	3.000	0.861	0.896	4.12
Hawkins	0.100	3.900	4.000	0.969	1.009	4.13
Macaskill&Bates	0.114	0.267	0.381	0.725	0.729	0.51
Macaskill&Bates	0.150	1.350	1.500	0.740	0.761	2.84
Macaskill&Bates	0.190	0.190	0.381	0.734	0.735	0.16
Macaskill&Bates	0.200	1.800	2.000	0.780	0.806	3.35
Macaskill&Bates	0.202	0.471	0.673	0.720	0.727	1.03
Macaskill&Bates	0.262	0.610	0.872	0.725	0.736	1.41
Macaskill&Bates	0.267	0.114	0.381	0.742	0.742	0.02
Macaskill&Bates	0.300	2.700	3.000	0.885	0.916	3.52
Macaskill&Bates	0.336	0.336	0.673	0.733	0.738	0.69
Macaskill&Bates	0.343	0.038	0.381	0.751	0.749	0.29
Macaskill&Bates	0.436	0.436	0.872	0.744	0.751	0.93
Macaskill&Bates	0.450	1.050	1.500	0.772	0.787	2.02
Macaskill&Bates	0.471	0.202	0.673	0.748	0.750	0.32
Hawkins	0.500	0.500	1.000	0.752	0.761	1.23
Hawkins	0.500	2.500	3.000	0.909	0.936	3.02
Hawkins	0.500	3.500	4.000	1.002	1.054	5.18
Macaskill&Bates	0.600	1.400	2.000	0.824	0.843	2.37
Macaskill&Bates	0.606	0.067	0.673	0.763	0.763	0.04
Macaskill&Bates	0.610	0.262	0.872	0.763	0.767	0.50
Macaskill&Bates	0.750	0.750	1.500	0.805	0.815	1.29
Macaskill&Bates	0.785	0.087	0.872	0.782	0.783	0.19

Table 3 (Continued). Activity Coefficient of HCl: HCl-KCl-H<sub>2</sub>O System @25° C.

Source	Stoichiometric Molality			$\gamma_{\pm, \text{st}}(\text{HCl})$		
	HCl	KCl	Ionic Strength	Data	Calc	% Abs. Dev.
Macaskill&Bates	0.900	2.100	3.000	0.961	0.981	2.04
Macaskill&Bates	1.000	1.001	2.000	0.871	0.885	1.51
Hawkins	1.000	2.000	3.000	0.963	0.993	3.12
Hawkins	1.000	3.000	4.000	1.102	1.117	1.40
Hawkins	1.000	4.000	5.000	1.213	1.249	2.97
Macaskill&Bates	1.050	0.450	1.500	0.840	0.846	0.71
Macaskill&Bates	1.350	0.150	1.500	0.877	0.879	0.22
Macaskill&Bates	1.400	0.600	2.000	0.923	0.931	0.84
Macaskill&Bates	1.500	1.500	3.000	1.047	1.058	1.09
Macaskill&Bates	1.800	0.200	2.000	0.979	0.982	0.34
Hawkins	2.000	1.000	3.000	1.123	1.132	0.83
Hawkins	2.000	2.000	4.000	1.270	1.274	0.28
Hawkins	2.000	3.000	5.000	1.422	1.424	0.11
Macaskill&Bates	2.100	0.900	3.000	1.145	1.148	0.31
Macaskill&Bates	2.700	0.300	3.000	1.256	1.255	0.09
Hawkins	3.000	1.000	4.000	1.483	1.479	0.29
Hawkins	3.000	2.000	5.000	1.660	1.653	0.45
Hawkins	4.000	1.000	5.000	2.005	1.954	2.54
Average						1.28

Table 4. Activity Coefficient of HCl: HCl-NaCl-H<sub>2</sub>O System @25° C.

Source	Stoichiometric Molality			$\gamma_{\pm, \text{st (HCl)}}$		
	HCl	NaCl	Ionic Strength	Data	Calc	% Abs. Dev.
Harned & Owen	0.01	0.01	0.02	0.874	0.874285	0.032604
Harned & Owen	0.01	0.02	0.03	0.854	0.85424	0.028082
Harned & Owen	0.01	0.05	0.06	0.818	0.816915	0.132701
Hawkins	0.01	0.09	0.1	0.785	0.788592	0.45758
Macaskill et al.	0.01	0.09	0.1	0.788818	0.788592	0.028706
Macaskill et al.	0.03	0.07	0.1	0.790631	0.789792	0.106159
Hawkins	0.05	0.05	0.1	0.786	0.790993	0.635281
Macaskill et al.	0.05	0.05	0.1	0.792133	0.790993	0.14382
Macaskill et al.	0.07	0.03	0.1	0.793466	0.792197	0.159959
Macaskill et al.	0.09	0.01	0.1	0.795074	0.793402	0.210284
Harned & Owen	0.01	0.1	0.11	0.784	0.783413	0.074813
Harned & Owen	0.01	0.2	0.21	0.752	0.751279	0.095846
Macaskill et al.	0.26663	0.11427	0.3809	0.748158	0.745987	0.29023
Macaskill et al.	0.03809	0.34281	0.3809	0.73414	0.732919	0.166336
Macaskill et al.	0.11427	0.26663	0.3809	0.739272	0.737248	0.273794
Macaskill et al.	0.19045	0.19045	0.3809	0.743854	0.741604	0.302532
Macaskill et al.	0.34281	0.03809	0.3809	0.752745	0.750397	0.311932
Harned & Owen	0.01	0.5	0.51	0.73	0.727838	0.296131
Macaskill et al.	0.06729	0.60561	0.6729	0.736903	0.733767	0.425605
Macaskill et al.	0.20187	0.47103	0.6729	0.744804	0.741461	0.448892
Macaskill et al.	0.33645	0.33645	0.6729	0.752344	0.749239	0.412683
Macaskill et al.	0.47103	0.20187	0.6729	0.760092	0.757102	0.393287
Macaskill et al.	0.60561	0.06729	0.6729	0.766988	0.765052	0.252323
Macaskill et al.	0.6104	0.2616	0.872	0.778255	0.7757	0.328297
Macaskill et al.	0.0872	0.7848	0.872	0.748952	0.744883	0.543357
Macaskill et al.	0.2616	0.6104	0.872	0.7589	0.75501	0.512556
Macaskill et al.	0.436	0.436	0.872	0.767179	0.765282	0.247333
Hawkins	0.01	0.99	1	0.765	0.749559	2.018438
Hawkins	0.1	0.9	1	0.766	0.754792	1.4632
Hawkins	0.5	0.5	1	0.782	0.778516	0.445498
Harned & Owen	0.01	1	1.01	0.754	0.750346	0.484638
Harned & Owen	0.01	2	2.01	0.878	0.869225	0.999456
Hawkins	0.01	2.99	3	1.085	1.052005	3.041039
Hawkins	0.1	2.9	3	1.084	1.059058	2.300927
Hawkins	0.5	2.5	3	1.106	1.091021	1.35432
Hawkins	1	2	3	1.135	1.132417	0.227574
Hawkins	2	1	3	1.224	1.220237	0.307441
Harned & Owen	0.011	3	3.011	1.068	1.054478	1.266147
Hawkins	0.1	3.9	4	1.33	1.31448	1.166883
Jiang	0.4	3.6	4	1.402329	1.343417	4.201052
Hawkins	0.5	3.5	4	1.367	1.353224	1.007725
Jiang	0.8	3.2	4	1.432617	1.383126	3.454561
Hawkins	1	3	4	1.416	1.403457	0.885816
Jiang	1.2	2.8	4	1.464468	1.424105	2.756202
Jiang	1.6	2.4	4	1.502139	1.466359	2.381909
Jiang	2	2	4	1.538934	1.509914	1.885734
Hawkins	2	2	4	1.521	1.509914	0.728875
Jiang	2.4	1.6	4	1.572679	1.554805	1.136515

Table 4 (Continued). Activity Coefficient of HCl: HCl-NaCl-H<sub>2</sub>O System @25° C.

Source	Stoichiometric Molality			$\gamma_{\pm, \text{st (HCl)}}$		
	HCl	NaCl	Ionic Strength	Data	Calc	% Abs. Dev.
Jiang	2.8	1.2	4	1.615437	1.601075	0.889041
Hawkins	3	1	4	1.624	1.624742	0.045666
Jiang	3.2	0.8	4	1.65238	1.648771	0.218444
Jiang	3.6	0.4	4	1.702433	1.697942	0.26381
Hawkins	0.1	4.9	5	1.683	1.649166	2.010314
Jiang	0.5	4.5	5	1.783282	1.697245	4.824625
Hawkins	0.5	4.5	5	1.724	1.697245	1.551901
Jiang	1	4	5	1.830923	1.760322	3.856025
Hawkins	1	4	5	1.778	1.760322	0.994273
Jiang	1.5	3.5	5	1.881612	1.825997	2.955677
Jiang	2	3	5	1.944554	1.893974	2.601133
Hawkins	2	3	5	1.908	1.893974	0.73514
Jiang	2.5	2.5	5	2.005349	1.964204	2.051773
Jiang	3	2	5	2.059729	2.036767	1.114782
Hawkins	3	2	5	2.046	2.036767	0.451265
Jiang	3.5	1.5	5	2.132996	2.111799	0.993743
Jiang	4	1	5	2.19427	2.18946	0.219214
Hawkins	4	1	5	2.199	2.18946	0.433855
Jiang	4.5	0.5	5	2.282969	2.269912	0.571909
Hawkins	0.1	5.9	6	2.145	2.015382	6.042791
Hawkins	0.5	5.5	6	2.197	2.084916	5.101667
Jiang	0.6	5.4	6	2.28681	2.10282	8.045685
Hawkins	1	5	6	2.263	2.176119	3.8392
Jiang	1.2	4.8	6	2.3595	2.213571	6.184766
Jiang	1.8	4.2	6	2.437923	2.328002	4.508789
Hawkins	2	4	6	2.435	2.366626	2.807982
Jiang	2.4	3.6	6	2.538809	2.444374	3.719632
Jiang	3	3	6	2.636089	2.562139	2.805273
Hawkins	3	3	6	2.599	2.562139	1.418272
Jiang	3.6	2.4	6	2.721949	2.68156	1.483812
Hawkins	4	2	6	2.799	2.762431	1.306496
Jiang	4.2	1.8	6	2.842955	2.803336	1.393596
Jiang	4.8	1.2	6	2.942456	2.928305	0.480923
Hawkins	5	1	6	2.998	2.970815	0.906787
Jiang	5.4	0.6	6	3.093285	3.057282	1.163927
Jiang	6.3	0.7	7	4.224157	4.129452	2.241969
Average						1.441181

Table 5. Activity Coefficient of HCl: HCl-KCl-NaCl-H<sub>2</sub>O System @25° C.

Stoichiometric Molality				$\gamma_{\pm, \text{st (HCl)}}$		
HCl	NaCl	KCl	Ionic Strength	Data*	Calc	% Dev. **
0.32	0.8	2.88	4.0	1.093	1.088	0.44
0.64	0.8	2.56	4.0	1.141	1.131	0.89
0.96	0.8	2.24	4.0	1.192	1.178	1.21
1.28	0.8	1.92	4.0	1.248	1.229	1.55
1.6	0.8	1.6	4.0	1.307	1.284	1.70
1.92	0.8	1.28	4.0	1.366	1.345	1.53
2.24	0.8	0.96	4.0	1.433	1.411	1.54
2.56	0.8	0.64	4.0	1.500	1.484	1.08
2.88	0.8	0.32	4.0	1.579	1.563	1.02
0.4	1	3.6	5.0	1.290	1.256	2.64
0.8	1	3.2	5.0	1.362	1.320	3.08
1.2	1	2.8	5.0	1.440	1.392	3.33
1.6	1	2.4	5.0	1.528	1.472	3.67
2	1	2	5.0	1.621	1.561	3.68
2.4	1	1.6	5.0	1.715	1.661	3.15
2.8	1	1.2	5.0	1.826	1.772	2.96
3.2	1	0.8	5.0	1.934	1.896	2.00
3.6	1	0.4	5.0	2.070	2.034	1.70
0.48	1.2	4.32	6.0	1.526	1.440	5.68
0.96	1.2	3.84	6.0	1.631	1.532	6.08
1.44	1.2	3.36	6.0	1.746	1.637	6.22
1.92	1.2	2.88	6.0	1.879	1.757	6.51
2.4	1.2	2.4	6.0	2.021	1.893	6.31
2.88	1.2	1.92	6.0	2.165	2.049	5.37
3.36	1.2	1.44	6.0	2.341	2.227	4.90
3.84	1.2	0.96	6.0	2.514	2.430	3.35
4.32	1.2	0.48	6.0	2.737	2.662	2.73
Average						3.12

\* From Jiang (1996b)

\*\* Calculated as 100\*(Data-Predicted)/Data.

Table 6. KCl Solubility in Aqueous HCl Solution @25° C.

Stoichiometric Molality *			KCl Solubility		
HCl	Saturation KCl	Ionic Strength	Data (K <sub>sp</sub> ) **	Calc (K <sub>ip</sub> ) ***	% Abs. Dev. ****
0.733	4.160	4.89	8.020	8.079	0.74
1.444	3.530	4.97	8.020	8.017	0.03
2.126	2.877	5.00	8.020	7.633	4.82
2.802	2.347	5.15	8.020	7.511	6.34
3.489	1.945	5.43	8.020	7.732	3.58
4.182	1.585	5.77	8.020	7.878	1.77
4.885	1.263	6.15	8.020	7.883	1.70
5.612	0.995	6.61	8.020	7.838	2.27
6.378	0.797	7.18	8.020	7.946	0.91
7.180	0.632	7.81	8.020	7.910	1.37
8.034	0.518	8.55	8.020	8.038	0.22
8.943	0.437	9.38	8.020	8.229	2.62
9.904	0.373	10.28	8.020	8.243	2.79
10.924	0.324	11.25	8.020	8.142	1.52
12.012	0.294	12.31	8.020	8.044	0.31
13.178	0.282	13.46	8.020	8.076	0.71
14.413	0.270	14.68	8.020	7.748	3.38
15.772	0.300	16.07	8.020	8.117	1.21
17.227	0.333	17.559	8.020	7.968	0.64
Average					2.02 <sup>a</sup>

\* From Linke & Seidell (1965, pg. 116).

\*\* The solubility product (thermodynamic equilibrium constant) for KCl at 25° C.

\*\*\* The ionic product calculated from the predicted equilibrium concentrations and activity coefficients of the K<sup>+</sup> and Cl<sup>-</sup> ions.

\*\*\*\* Calculated as  $100 \cdot \text{abs}(K_{sp} - K_{ip}) / K_{sp}$ .

<sup>a</sup> The data in the last row (shaded) was not used to regress parameters and is not included in the average.



Table 7. NaCl Solubility in Aqueous HCl Solution @25° C.

Original Source	Stoichiometric Molality *			NaCl Solubility		
	HCl	Saturation NaCl	Ionic Strength	Data (K <sub>sp</sub> )**	Calc (K <sub>ip</sub> )***	% Abs. Dev. ****
Druzhinin & Shepelev	0	6.14	6.14	38.18	38.20	0.04
Ingham	0	6.17	6.17	38.18	38.84	1.71
Armstrong & Eyre	0	6.18	6.18	38.18	38.99	2.10
Armstrong & Eyre	0.25	5.89	6.15	38.18	37.12	2.79
Armstrong & Eyre	0.50	5.94	6.44	38.18	41.85	9.60
Ingham	0.57	5.53	6.10	38.18	35.92	5.93
Ingham	1.00	5.07	6.07	38.18	36.00	5.71
Armstrong & Eyre	1.00	5.10	6.10	38.18	36.52	4.37
Ingham	2.56	3.56	6.12	38.18	38.58	1.04
Ingham	3.60	2.61	6.22	38.18	38.57	1.02
Ingham	3.95	2.35	6.30	38.18	39.20	2.65
Ingham	4.33	2.03	6.37	38.18	38.36	0.46
Armstrong & Eyre	5.01	1.53	6.55	38.18	36.70	3.89
Ingham	5.13	1.52	6.64	38.18	38.73	1.42
Ingham	6.03	1.04	7.07	38.18	38.90	1.87
Ingham	7.08	0.63	7.71	38.18	38.51	0.86
Ingham	8.36	0.35	8.70	38.18	39.77	4.15
Ingham	9.61	0.19	9.80	38.18	39.20	2.65
Ingham	11.49	0.11	11.60	38.18	46.34	21.36
Ingham	18.97	0.02	18.99	38.18	38.85	1.74
Average						4.21†

\* From Linke & Seidell (1965, pp. 962-963, several original sources).

\*\* The solubility product (thermodynamic equilibrium constant) for NaCl at 25° C.

\*\*\* The ionic product calculated from the predicted equilibrium concentrations and activity coefficients of the Na<sup>+</sup> and Cl<sup>-</sup> ions.

\*\*\*\* Calculated as  $100 \cdot \text{abs}(K_{\text{sp}} - K_{\text{ip}}) / K_{\text{sp}}$ .

† Excludes the first three points where concentration of HCl = 0 (i.e., pure aqueous NaCl).

Table 8. KCl &amp; NaCl Solubility in Aqueous HCl Solution @25° C.

Stoichiometric Molality *				KCl Solubility			NaCl Solubility		
HCl	Saturation KCl	Saturation NaCl	Ionic Strength	Data (K <sub>sp</sub> )**	Calc (K <sub>ip</sub> ) ***	% Abs. Dev. ****	Data (K <sub>sp</sub> )**	Calc (K <sub>ip</sub> ) ***	% Abs. Dev. ****
3.23	1.39	2.49	7.11	8.02	8.124894	1.31	38.18	37.52	1.75
6.24	0.68	0.81	7.72	8.02	7.283686	9.18	38.18	34.81	8.83
7.61	0.52	0.47	8.59	8.02	7.602136	5.20	38.18	38.61	1.11
13.67	0.26	0.05	13.98	8.02	7.492992	6.57	38.18	32.58	14.69
Average						5.57	Average		6.60

\* From Linke & Seidell (1965, pp. 146-148). Both salts are at saturation.

\*\* The solubility product (thermodynamic equilibrium constant) for KCl or NaCl at 25° C.

\*\*\* The ionic product calculated from the predicted equilibrium concentrations and activity coefficients of the (Na<sup>+</sup> or K<sup>+</sup>) and Cl<sup>-</sup> ions.

\*\*\*\* Calculated as  $100 \cdot \text{abs}(K_{sp} - K_{ip}) / K_{sp}$ .

Table 9. HCl Partial Pressure: HCl-KCl-NaCl-H<sub>2</sub>O System @25° C.

Stoichiometric Molality			HCl Partial Pressure (atm)		
HCl	NaCl	KCl	Data*	Calc	% Abs. Dev.
1.5	3.5	0	1.28E-05	1.23E-05	4.00
1.5	2.8	0.7	1.03E-05	1.08E-05	4.73
1.5	2.1	1.4	8.89E-06	9.47E-06	6.54
1.5	1.4	2.1	7.66E-06	8.34E-06	8.83
1.5	0.7	2.8	7.11E-06	7.36E-06	3.53
1.5	0	3.5	6.14E-06	6.52E-06	6.23
Average					5.64

\* From Clegg & Brimblecombe (1988b, System 5).

Table 10.  $\gamma_{\pm, \text{st}}(\text{HCl})$  in Aqueous Sodium Chloride: 0-50° C (Excluding 25°).

Stoichiometric Molality			$\gamma_{\pm, \text{st}}(\text{HCl})$		
T (C)	HCl	NaCl	Data*	Calc	% Abs. Dev.
0	0.01	0.01	0.877	0.878	0.164
0	0.01	0.02	0.856	0.859	0.334
0	0.01	0.05	0.821	0.822	0.154
0	0.01	0.1	0.789	0.789	0.037
0	0.01	0.2	0.758	0.758	0.058
0	0.01	0.5	0.738	0.735	0.438
0	0.01	1	0.765	0.759	0.765
0	0.01	2	0.898	0.886	1.312
0	0.011	3	1.103	1.088	1.322
5	0.01	0.01	0.876	0.878	0.195
5	0.01	0.02	0.856	0.858	0.242
5	0.01	0.05	0.821	0.821	0.051
5	0.01	0.1	0.789	0.788	0.071
5	0.01	0.2	0.758	0.757	0.160
5	0.01	0.5	0.737	0.734	0.375
5	0.01	1	0.764	0.759	0.687
5	0.01	2	0.896	0.885	1.210
5	0.011	3	1.099	1.085	1.280
10	0.01	0.01	0.876	0.877	0.104
10	0.01	0.02	0.856	0.857	0.139
10	0.01	0.05	0.821	0.820	0.070
10	0.01	0.1	0.788	0.787	0.079
10	0.01	0.2	0.757	0.756	0.170
10	0.01	0.5	0.736	0.733	0.384
10	0.01	1	0.762	0.758	0.588
10	0.01	2	0.893	0.883	1.157
10	0.011	3	1.094	1.079	1.332
15	0.01	0.01	0.875	0.876	0.113
15	0.01	0.02	0.855	0.856	0.136
15	0.01	0.05	0.819	0.819	0.025
15	0.01	0.1	0.786	0.786	0.002
15	0.01	0.2	0.754	0.754	0.029
15	0.01	0.5	0.733	0.731	0.211
15	0.01	1	0.759	0.755	0.486
15	0.01	2	0.888	0.879	1.058
15	0.011	3	1.086	1.072	1.315
20	0.01	0.01	0.874	0.875	0.127
20	0.01	0.02	0.855	0.855	0.020
20	0.01	0.05	0.819	0.818	0.118
20	0.01	0.1	0.785	0.785	0.039
20	0.01	0.2	0.753	0.753	0.035
20	0.01	0.5	0.732	0.730	0.319
20	0.01	1	0.756	0.753	0.411
20	0.01	2	0.883	0.874	1.010
20	0.011	3	1.077	1.063	1.268
30	0.01	0.01	0.873	0.873	0.010
30	0.01	0.02	0.853	0.853	0.016

Table 10 (Continued).  $\gamma_{\pm, \text{st}}(\text{HCl})$  in Aqueous Sodium Chloride: 0-50° C (Excluding 25°).

Stoichiometric Molality			$\gamma_{\pm, \text{st}}(\text{HCl})$		
T (C)	HCl	NaCl	Data*	Calc	% Abs. Dev.
30	0.01	0.05	0.816	0.815	0.096
30	0.01	0.1	0.781	0.781	0.052
30	0.01	0.2	0.749	0.749	0.014
30	0.01	0.5	0.727	0.725	0.314
30	0.01	1	0.750	0.746	0.528
30	0.01	2	0.871	0.862	1.061
30	0.011	3	1.056	1.042	1.321
35	0.01	0.01	0.872	0.872	0.003
35	0.01	0.02	0.851	0.852	0.069
35	0.01	0.05	0.814	0.814	0.044
35	0.01	0.1	0.779	0.780	0.069
35	0.01	0.2	0.747	0.747	0.045
35	0.01	0.5	0.724	0.722	0.312
35	0.01	1	0.746	0.742	0.554
35	0.011	2	0.864	0.855	1.088
35	0.011	3	1.043	1.030	1.271
40	0.01	0.01	0.871	0.871	0.022
40	0.01	0.02	0.850	0.850	0.030
40	0.01	0.05	0.812	0.812	0.004
40	0.01	0.1	0.777	0.778	0.070
40	0.01	0.2	0.745	0.744	0.098
40	0.01	0.5	0.721	0.719	0.346
40	0.01	1	0.742	0.737	0.633
40	0.011	2	0.856	0.847	1.097
40	0.011	3	1.029	1.017	1.205
45	0.01	0.01	0.870	0.870	0.047
45	0.01	0.02	0.849	0.849	0.017
45	0.01	0.05	0.810	0.810	0.028
45	0.01	0.1	0.774	0.775	0.187
45	0.01	0.2	0.742	0.742	0.036
45	0.01	0.5	0.718	0.715	0.411
45	0.01	1	0.738	0.732	0.757
45	0.011	2	0.847	0.838	1.051
45	0.011	3	1.014	1.003	1.108
50	0.01	0.01	0.869	0.868	0.078
50	0.01	0.02	0.847	0.847	0.046
50	0.01	0.05	0.807	0.808	0.171
50	0.01	0.1	0.771	0.773	0.289
50	0.01	0.2	0.739	0.739	0.005
50	0.01	0.5	0.715	0.711	0.510
50	0.01	1	0.733	0.727	0.794
50	0.011	2	0.838	0.829	1.066
50	0.011	3	0.999	0.988	1.076
Average					0.418

\* From Harned &amp; Owen (1958)

Table 11. NaCl Solubility in Aqueous Hydrochloric Acid: 0-30° C (Excluding 25°).

Original Source	T (C)	Stoichiometric Molality*			NaCl Solubility		
		HCl	Saturation NaCl	Ionic Strength	Data ( $K_{sp}$ )**	Calc ( $K_{ip}$ )***	% Abs. Dev. ****
Engel	0	0.113	6.060	6.173	31.540	32.723	3.75
Engel	0	0.208	5.886	6.094	31.540	31.146	1.25
Armstrong & Eyre	0	0.251	5.848	6.099	31.540	31.202	1.07
Armstrong & Eyre	0	0.501	5.547	6.049	31.540	30.565	3.09
Engel	0	0.573	5.461	6.034	31.540	30.447	3.46
Armstrong & Eyre	0	1.003	4.982	5.985	31.540	30.582	3.04
Engel	0	1.041	4.937	5.978	31.540	30.561	3.10
Engel	0	1.687	4.256	5.943	31.540	31.327	0.68
Engel	0	3.457	2.638	6.095	31.540	34.455	9.24
Engel	0	6.444	0.705	7.148	31.540	32.117	1.83
Seidel & Fischer	0	8.129	0.258	8.387	31.540	29.233	7.31
Seidel & Fischer	0	10.047	0.096	10.143	31.540	31.035	1.60
Seidel & Fischer	0	17.549	0.013	17.562	31.540	30.808	2.32
Average @0° C							3.21
Fricke & Brummer	18	0.059	6.071	6.131	36.684	36.588	0.26
Fricke & Brummer	18	0.118	6.009	6.127	36.684	36.250	1.18
Fricke & Brummer	18	0.237	5.876	6.114	36.684	35.657	2.80
Fricke & Brummer	18	0.485	5.577	6.063	36.684	34.590	5.71
Fricke & Brummer	18	1.226	4.771	5.997	36.684	34.506	5.94
Fricke & Brummer	18	2.165	3.750	5.915	36.684	33.974	7.39
Fricke & Brummer	18	3.418	2.627	6.044	36.684	34.914	4.83
Fricke & Brummer	18	4.529	1.788	6.316	36.684	35.281	3.83
Average @18° C							3.99
Masson	30	0.517	5.569	6.085	39.073	35.856	8.24
Masson	30	1.091	4.937	6.027	39.073	35.268	9.74
Masson	30	2.010	4.040	6.050	39.073	36.660	6.18
Schreinemakers	30	2.471	3.595	6.067	39.073	37.008	5.29
Masson	30	2.713	3.349	6.062	39.073	36.660	6.18
Masson	30	3.439	2.775	6.214	39.073	38.602	1.21
Schreinemakers	30	4.387	2.047	6.434	39.073	39.181	0.27
Masson	30	4.706	1.845	6.551	39.073	39.879	2.06
Schreinemakers	30	6.091	0.990	7.080	39.073	36.517	6.54
Masson	30	6.878	0.728	7.607	39.073	39.095	0.06
Masson	30	8.502	0.316	8.818	39.073	36.858	5.67
Schreinemakers	30	15.187	0.029	15.216	39.073	24.464	37.39
Average @30° C							7.4
Total Average							4.92

\* From Linke &amp; Seidell (1965, pp. 962-963, several original sources).

\*\* The solubility product (thermodynamic equilibrium constant) for NaCl at 25° C.

\*\*\* The ionic product calculated from the predicted equilibrium concentrations and activity coefficients of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions.\*\*\*\* Calculated as  $100 \cdot \text{abs}(K_{sp} - K_{ip}) / K_{sp}$ .

Table 12. KCl Solubility in Aqueous HCl Solution @0° C.

Stoichiometric Molality *			KCl Solubility		
HCl	Saturation KCl	Ionic Strength	Data (K <sub>sp</sub> ) **	Calc (K <sub>ip</sub> ) ***	% Abs. Dev. ****
0.000	3.828	3.828	4.327	4.100	5.24
0.690	3.121	3.811	4.327	3.893	10.04
1.358	2.523	3.881	4.327	3.799	12.20
2.019	2.057	4.076	4.327	3.874	10.48
2.679	1.654	4.333	4.327	3.949	8.75
3.345	1.309	4.653	4.327	3.994	7.69
4.023	1.017	5.040	4.327	3.983	7.94
4.740	0.828	5.568	4.327	4.182	3.35
5.492	0.688	6.180	4.327	4.436	2.52
6.281	0.580	6.861	4.327	4.690	8.40
7.105	0.487	7.592	4.327	4.823	11.47
7.971	0.408	8.378	4.327	4.826	11.53
8.871	0.325	9.197	4.327	4.480	3.53
9.836	0.278	10.113	4.327	4.303	0.56
10.862	0.247	11.109	4.327	4.210	2.72
11.942	0.214	12.156	4.327	3.990	7.79
13.099	0.200	13.299	4.327	3.992	7.73
14.346	0.206	14.553	4.327	4.246	1.88
15.672	0.213	15.885	4.327	4.332	0.11
17.113	0.242	17.356	4.327	4.522	4.50
18.689	0.297	18.986	4.327	4.585	5.97
20.424	0.381	20.805	4.327	4.221	2.45
22.306	0.471	22.777	4.327	3.223	25.52
Average					6.42 <sup>a</sup>

\* From Linke & Seidell (1965, pg. 116).

\*\* The solubility product (thermodynamic equilibrium constant) for KCl at 0° C.

\*\*\* The ionic product calculated from the predicted equilibrium concentrations and activity coefficients of the K<sup>+</sup> and Cl<sup>-</sup> ions.

\*\*\*\* Calculated as  $100 \cdot \text{abs}(K_{\text{sp}} - K_{\text{ip}}) / K_{\text{sp}}$ .

<sup>a</sup> The data in the shaded rows were not used to regress parameters and are not included in the average.

Table 13.  $\gamma_{\pm, \text{st}}(\text{HCl})$  Of Dilute HCl In Aqueous Potassium Chloride: 0-50° C.

T (C)	Stoichiometric Molality		$\gamma_{\pm, \text{st}}(\text{HCl})$		
	HCl	KCl	Data*	Calc	% Abs. Dev.
0	0.01	0.01	0.876	0.878	0.21
0	0.01	0.02	0.856	0.858	0.20
0	0.01	0.03	0.841	0.842	0.16
0	0.01	0.05	0.819	0.820	0.09
0	0.01	0.1	0.786	0.785	0.13
0	0.01	0.2	0.753	0.750	0.36
0	0.01	0.5	0.712	0.720	1.12
0	0.01	1	0.731	0.729	0.27
0	0.01	1.5	0.758	0.760	0.32
0	0.01	2	0.801	0.802	0.09
0	0.01	3	0.893	0.900	0.76
0	0.01	3.5	0.939	0.953	1.51
0° Average					0.43
5	0.01	0.01	0.875	0.877	0.24
5	0.01	0.02	0.855	0.857	0.22
5	0.01	0.03	0.841	0.842	0.07
5	0.01	0.05	0.819	0.819	0.01
5	0.01	0.1	0.786	0.784	0.25
5	0.01	0.2	0.753	0.749	0.47
5	0.01	0.5	0.712	0.719	1.01
5	0.01	1	0.727	0.728	0.17
5	0.01	1.5	0.757	0.760	0.35
5	0.01	3	0.890	0.900	1.10
5	0.01	3.5	0.933	0.954	2.23
5° Average					0.56
10	0.01	0.01	0.875	0.876	0.15
10	0.01	0.02	0.853	0.856	0.36
10	0.01	0.03	0.840	0.841	0.08
10	0.01	0.05	0.817	0.818	0.11
10	0.01	0.1	0.786	0.783	0.38
10	0.01	0.2	0.752	0.748	0.48
10	0.01	0.5	0.711	0.718	0.99
10	0.01	1	0.728	0.727	0.15
10	0.01	1.5	0.754	0.758	0.55
10	0.01	2	0.796	0.800	0.44
10	0.01	3	0.882	0.899	1.88
10	0.01	3.5	0.926	0.953	2.91
10° Average					0.71
15	0.01	0.01	0.874	0.875	0.16
15	0.01	0.02	0.853	0.855	0.24
15	0.01	0.03	0.839	0.840	0.07
15	0.01	0.05	0.817	0.817	0.03
15	0.01	0.1	0.784	0.782	0.29
15	0.01	0.2	0.750	0.747	0.41
15	0.01	0.5	0.709	0.716	1.03
15	0.01	1	0.725	0.725	0.02
15	0.01	1.5	0.750	0.756	0.77
15	0.01	2	0.791	0.797	0.74

Table 13 (Continued).  $\gamma_{\pm, \text{st}}(\text{HCl})$  Of Dilute HCl In Aqueous Potassium Chloride: 0-50° C.

T (C)	Stoichiometric Molality		$\gamma_{\pm, \text{st}}(\text{HCl})$		
	HCl	KCl	Data*	Calc	% Abs. Dev.
15	0.01	3	0.875	0.896	2.37
15	0.01	3.5	0.917	0.950	3.63
15° Average					0.81
20	0.01	0.01	0.874	0.875	0.06
20	0.01	0.02	0.853	0.854	0.12
20	0.01	0.03	0.838	0.839	0.06
20	0.01	0.05	0.816	0.816	0.05
20	0.01	0.1	0.783	0.780	0.32
20	0.01	0.2	0.749	0.746	0.46
20	0.01	0.5	0.708	0.715	0.94
20	0.01	1	0.723	0.723	0.03
20	0.01	1.5	0.747	0.753	0.83
20	0.01	2	0.786	0.794	1.01
20	0.01	3	0.868	0.893	2.83
20	0.01	3.5	0.908	0.947	4.32
20° Average					0.92
25	0.01	0.01	0.874	0.874	0.03
25	0.01	0.02	0.852	0.853	0.14
25	0.01	0.03	0.837	0.838	0.07
25	0.01	0.05	0.816	0.815	0.18
25	0.01	0.1	0.782	0.779	0.35
25	0.01	0.2	0.747	0.744	0.37
25	0.01	0.5	0.706	0.713	1.00
25	0.01	1	0.720	0.721	0.09
25	0.01	1.5	0.743	0.751	1.02
25	0.01	2	0.781	0.791	1.28
25	0.01	3	0.860	0.889	3.38
25	0.01	3.5	0.899	0.944	4.98
25° Average					1.07
30	0.01	0.01	0.873	0.873	0.05
30	0.01	0.02	0.851	0.852	0.09
30	0.01	0.03	0.836	0.836	0.01
30	0.01	0.05	0.814	0.813	0.14
30	0.01	0.1	0.780	0.777	0.34
30	0.01	0.2	0.746	0.742	0.54
30	0.01	0.5	0.704	0.710	0.88
30	0.01	1	0.716	0.717	0.12
30	0.01	1.5	0.738	0.746	1.09
30	0.01	2	0.773	0.786	1.64
30	0.01	3	0.851	0.883	3.72
30	0.01	3.5	0.888	0.937	5.52
30° Average					1.18
35	0.01	0.01	0.871	0.871	0.05
35	0.01	0.02	0.850	0.851	0.07
35	0.01	0.03	0.834	0.835	0.09
35	0.01	0.05	0.812	0.811	0.08
35	0.01	0.1	0.778	0.776	0.31



Table 13 (Continued).  $\gamma_{\pm, \text{st}}(\text{HCl})$  Of Dilute HCl In Aqueous Potassium Chloride: 0-50° C.

T (C)	Stoichiometric Molality		$\gamma_{\pm, \text{st}}(\text{HCl})$		
	HCl	KCl	Data*	Calc	% Abs. Dev.
35	0.01	0.2	0.743	0.740	0.42
35	0.01	0.5	0.701	0.707	0.92
35	0.01	1	0.712	0.713	0.19
35	0.01	1.5	0.732	0.742	1.33
35	0.01	2	0.767	0.781	1.77
35	0.01	3	0.841	0.876	4.21
35	0.01	3.5	0.876	0.930	6.20
35° Average					1.30
40	0.01	0.01	0.871	0.870	0.08
40	0.01	0.02	0.850	0.849	0.09
40	0.01	0.03	0.834	0.833	0.08
40	0.01	0.05	0.812	0.810	0.27
40	0.01	0.1	0.777	0.774	0.42
40	0.01	0.2	0.742	0.738	0.58
40	0.01	0.5	0.699	0.705	0.79
40	0.01	1	0.709	0.709	0.06
40	0.01	1.5	0.728	0.737	1.22
40	0.01	2	0.761	0.775	1.83
40	0.01	3	0.831	0.869	4.61
40	0.01	3.5	0.867	0.923	6.42
40° Average					1.37
45	0.01	0.01	0.869	0.869	0.01
45	0.01	0.02	0.847	0.848	0.10
45	0.01	0.03	0.831	0.832	0.10
45	0.01	0.05	0.809	0.808	0.11
45	0.01	0.1	0.773	0.772	0.17
45	0.01	0.2	0.739	0.735	0.50
45	0.01	0.5	0.695	0.701	0.92
45	0.01	1	0.702	0.705	0.46
45	0.01	1.5	0.722	0.732	1.35
45	0.01	2	0.753	0.769	2.10
45	0.01	3	0.820	0.862	5.07
45	0.01	3.5	0.853	0.914	7.18
45° Average					1.51
50	0.01	0.01	0.866	0.868	0.21
50	0.01	0.02	0.844	0.846	0.29
50	0.01	0.03	0.828	0.830	0.27
50	0.01	0.05	0.806	0.806	0.04
50	0.01	0.1	0.769	0.770	0.08
50	0.01	0.2	0.734	0.733	0.17
50	0.01	0.5	0.690	0.698	1.17
50	0.01	1	0.697	0.701	0.53
50	0.01	1.5	0.713	0.726	1.84
50	0.01	2	0.743	0.762	2.58
50	0.01	3	0.808	0.853	5.58
50	0.01	3.5	0.839	0.905	7.87
50° Average					1.72
Global Average					1.06

\* From Harned &amp; Owen (1958, pg. 748)

Table 14. Nitric Acid Dissociation Constant.

T (C)	Eq. [14]	Sources of Used Dissociation Data	Other Literature Sources	
0	26.92	40-48 Hood & Reilly (1960)	45.39 39.81	Marshall & Slusher (1975) Sillen & Martell (1964)
25	17.92	25-27.5 Hood & Reilly (1960) 23.5 Krawetz (1955) 18.8 Davis & De Bruin (1964)	173.8 - 195 33.88 25.03 21, 22 1.2 - 25.12	Sampoli et al. (1985) Sillen & Martell (1971) Marshall & Slusher (1975) Hood et al. (1954) Sillen & Martell (1964)
70	10.00	12.5-15 Hood & Reilly (1960)	12.59 8.28	Sillen & Martell (1964) Marshall & Slusher (1975)

Table 15. Nitric Acid Dissociation Results &amp; Data.

Source	T (C)	Stoich. HNO <sub>3</sub> Molality	Extent of Dissociation		
			Data	Model	% Abs. Dev.
Hood & Reilly	0	1.03	0.988	0.983	0.50
Hood & Reilly	0	2.14	0.974	0.966	0.81
Hood & Reilly	0	3.31	0.950	0.945	0.55
Hood & Reilly	0	4.57	0.923	0.917	0.70
Hood & Reilly	0	7.41	0.840	0.834	0.73
Hood & Reilly	0	10.84	0.710	0.720	1.40
Hood & Reilly	0	14.81	0.614	0.598	2.61
Hood & Reilly	0	20.66	0.445	0.446	0.22
					0.94
Davis & de Bruin	25	0.01	1.000	1.000	0.00
Davis & de Bruin	25	0.01	0.999	1.000	0.01
Davis & de Bruin	25	0.02	0.999	0.999	0.01
Davis & de Bruin	25	0.05	0.998	0.998	0.03
Davis & de Bruin	25	0.10	0.996	0.997	0.05
Davis & de Bruin	25	0.20	0.993	0.994	0.07
Davis & de Bruin	25	0.51	0.985	0.986	0.08
Davis & de Bruin	25	0.72	0.980	0.981	0.10
Krawetz	25	0.85	0.995	0.978	1.73
Davis & de Bruin	25	1.03	0.973	0.974	0.05
Hood & Reilly	25	1.03	0.985	0.974	1.17
Davis & de Bruin	25	1.57	0.961	0.960	0.07
Krawetz	25	1.59	0.981	0.960	2.14
Davis & de Bruin	25	2.13	0.948	0.946	0.24
Hood & Reilly	25	2.14	0.958	0.945	1.31
Krawetz	25	2.43	0.946	0.937	0.92
Davis & de Bruin	25	2.71	0.933	0.929	0.41
Davis & de Bruin	25	3.30	0.914	0.910	0.40
Hood & Reilly	25	3.31	0.929	0.910	2.05
Krawetz	25	3.47	0.912	0.905	0.79
Davis & de Bruin	25	3.92	0.892	0.889	0.33
Krawetz	25	4.54	0.878	0.866	1.36
Davis & de Bruin	25	4.56	0.866	0.865	0.07
Hood & Reilly	25	4.57	0.880	0.865	1.72
Davis & de Bruin	25	5.22	0.839	0.840	0.06
Krawetz	25	5.64	0.814	0.823	1.07
Davis & de Bruin	25	5.91	0.809	0.812	0.34
Davis & de Bruin	25	6.64	0.780	0.783	0.33
Davis & de Bruin	25	7.39	0.748	0.752	0.58
Hood & Reilly	25	7.41	0.775	0.752	3.01
Davis & de Bruin	25	8.18	0.716	0.721	0.76
Krawetz	25	8.36	0.705	0.714	1.34
Davis & de Bruin	25	9.01	0.682	0.690	1.21
Krawetz	25	9.84	0.664	0.661	0.52
Davis & de Bruin	25	9.88	0.651	0.659	1.24
Davis & de Bruin	25	10.80	0.620	0.628	1.29
Hood & Reilly	25	10.84	0.632	0.627	0.83
Krawetz	25	10.94	0.644	0.624	3.18
Davis & de Bruin	25	11.77	0.589	0.597	1.38

Table 15. (Continued) Nitric Acid Dissociation Results &amp; Data.

Source	T (C)	Stoich. HNO <sub>3</sub> Molality	Extent of Dissociation		
			Data	Model	% Abs. Dev.
Davis & de Bruin	25	12.80	0.559	0.567	1.34
Krawetz	25	13.30	0.553	0.552	0.13
Davis & de Bruin	25	13.89	0.530	0.536	1.16
Krawetz	25	14.56	0.514	0.518	0.85
Hood & Reilly	25	14.81	0.546	0.512	6.24
Davis & de Bruin	25	15.05	0.501	0.506	0.98
Krawetz	25	15.79	0.478	0.488	2.05
Davis & de Bruin	25	17.62	0.441	0.445	1.01
Krawetz	25	18.68	0.414	0.423	2.07
Krawetz	25	20.06	0.387	0.394	1.87
Davis & de Bruin	25	20.59	0.381	0.384	0.72
Hood & Reilly	25	20.66	0.386	0.382	0.91
					1.01
Hood & Reilly	70	1.03	0.974	0.953	2.11
Hood & Reilly	70	2.14	0.925	0.902	2.53
Hood & Reilly	70	3.31	0.876	0.838	4.30
Hood & Reilly	70	4.57	0.806	0.768	4.77
Hood & Reilly	70	7.41	0.680	0.629	7.56
Hood & Reilly	70	10.84	0.548	0.510	7.00
Hood & Reilly	70	14.81	0.450	0.415	7.68
Hood & Reilly	70	20.66	0.318	0.320	0.73
					4.58
Global Average					1.43

Table 16. Nitric Acid Osmotic &amp; Activity Coefficients @25° C.

Source	Stoich. HNO <sub>3</sub> Molality	$\gamma_{\pm, \text{st}}(\text{HNO}_3)$			$\phi_{\text{st}}$		
		Data	Model	% Abs. Dev.	Data	Model	% Abs. Dev.
Redlich et al.	0.001	0.966	0.965	0.02			
Hamer&Wu	0.001	0.965	0.965	0.04	0.989	0.989	0.04
Hamer&Wu	0.002	0.952	0.952	0.04	0.984	0.984	0.04
Redlich et al.	0.005	0.928	0.929	0.10			
Hamer&Wu	0.005	0.929	0.929	0.03	0.977	0.977	0.02
Hamer&Wu	0.010	0.905	0.905	0.01	0.969	0.969	0.04
Redlich et al.	0.020	0.868	0.876	0.94			
Hamer&Wu	0.020	0.875	0.876	0.10	0.961	0.961	0.01
Hamer&Wu	0.050	0.829	0.831	0.20	0.948	0.949	0.12
Hamer&Wu	0.100	0.792	0.794	0.28	0.941	0.942	0.12
Redlich et al.	0.100	0.785	0.794	1.18			
Hamer&Wu	0.200	0.756	0.760	0.55	0.937	0.940	0.28
Hamer&Wu	0.300	0.739	0.744	0.62	0.940	0.942	0.19
Hamer&Wu	0.400	0.730	0.734	0.59	0.944	0.946	0.16
Hamer&Wu	0.500	0.725	0.729	0.56	0.949	0.950	0.11
Redlich et al.	0.500	0.715	0.729	2.02			
Hamer&Wu	0.600	0.723	0.726	0.47	0.955	0.955	0.00
Hamer&Wu	0.700	0.723	0.725	0.34	0.961	0.960	0.08
Hamer&Wu	0.800	0.724	0.726	0.25	0.968	0.966	0.24
Hamer&Wu	0.900	0.727	0.727	0.03	0.975	0.971	0.37
Hamer&Wu	1.000	0.730	0.730	0.06	0.981	0.977	0.38
Redlich et al.	1.000	0.720	0.730	1.34			
Redlich et al.	1.133	0.725	0.734	1.22			
Hamer&Wu	1.200	0.738	0.736	0.25	0.995	0.989	0.57
Hamer&Wu	1.400	0.749	0.745	0.55	1.009	1.002	0.70
Hamer&Wu	1.600	0.761	0.755	0.73	1.023	1.015	0.80
Hamer&Wu	1.800	0.774	0.767	0.85	1.036	1.028	0.76
Hamer&Wu	2.000	0.788	0.781	0.92	1.050	1.042	0.80
Redlich et al.	2.313	0.806	0.804	0.27			
Hamer&Wu	2.500	0.826	0.819	0.89	1.083	1.076	0.64
Hamer&Wu	3.000	0.868	0.862	0.68	1.114	1.111	0.29
Hamer&Wu	3.500	0.913	0.910	0.36	1.145	1.145	0.00
Redlich et al.	3.543	0.927	0.914	1.41			
Hamer&Wu	4.000	0.961	0.961	0.02	1.175	1.178	0.26
Hamer&Wu	4.500	1.011	1.014	0.34	1.203	1.210	0.55
Redlich et al.	4.827	1.051	1.051	0.09			
Hamer&Wu	5.000	1.063	1.070	0.65	1.230	1.239	0.75
Hamer&Wu	5.500	1.116	1.127	0.97	1.256	1.267	0.87
Hamer&Wu	6.000	1.171	1.185	1.16	1.281	1.293	0.90
Redlich et al.	6.167	1.203	1.204	0.09			
Hamer&Wu	7.000	1.285	1.302	1.29	1.327	1.338	0.84
Hamer&Wu	8.000	1.403	1.419	1.16	1.368	1.377	0.65
Hamer&Wu	9.000	1.523	1.537	0.91	1.405	1.410	0.37
Hamer&Wu	10.000	1.644	1.654	0.61	1.437	1.439	0.13
Redlich et al.	10.573	1.731	1.721	0.60			
Hamer&Wu	11.000	1.765	1.770	0.28	1.465	1.464	0.09
Hamer&Wu	12.000	1.884	1.884	0.03	1.488	1.485	0.20

Table 16 (Continued). Nitric Acid Osmotic &amp; Activity Coefficients @25° C.

Source	Stoich. HNO <sub>3</sub> Molality	$\gamma_{\pm, \text{st}}(\text{HNO}_3)$			$\phi_{\text{st}}$		
		Data	Model	% Abs. Dev.	Data	Model	% Abs. Dev.
Hamer&Wu	13.000	1.999	1.997	0.11	1.508	1.503	0.31
Hamer&Wu	14.000	2.109	2.106	0.15	1.523	1.519	0.29
Hamer&Wu	15.000	2.212	2.211	0.06	1.535	1.531	0.26
Hamer&Wu	16.000	2.309	2.310	0.04	1.543	1.540	0.17
Hamer&Wu	17.000	2.397	2.402	0.22	1.547	1.547	0.02
Hamer&Wu	18.000	2.476	2.486	0.41	1.548	1.550	0.10
Hamer&Wu	19.000	2.546	2.560	0.54	1.546	1.549	0.20
Hamer&Wu	20.000	2.607	2.622	0.56	1.542	1.545	0.18
Average				0.51			0.32

Table 17. Multi-temperature HNO<sub>3</sub> Partial Pressure @1 atm. Total Pressure: Model vs. Data.

T(C)	Stoich. HNO <sub>3</sub> Molality	HNO <sub>3</sub> Partial Pressure				
		Data* (atm)	Model Prediction		% Absolute Deviation	
			Isothermal Regression	Transformed CB	Isothermal Regression	Transformed CB
106.4	5.89	9.500E-03	6.415E-03	5.311E-03	32.47	44.09
107.8	7.36	1.500E-02	1.126E-02	9.361E-03	24.92	37.59
109.4	8.96	2.110E-02	1.886E-02	1.576E-02	10.60	25.33
111.8	11.77	4.230E-02	3.863E-02	3.253E-02	8.68	23.10
112.3	12.43	5.100E-02	4.456E-02	3.760E-02	12.62	26.28
114.8	16.12	8.950E-02	8.768E-02	7.469E-02	2.04	16.54
116.85	20.12	1.360E-01	1.525E-01	1.310E-01	12.10	3.65
Average					14.77	25.23

\* From Ellis & Thwaites (1957)

Table 18. Pitzer Parameters and Equilibrium Constants For Chloride System Taken From Literature.

Pitzer Parameters ( Values for Eq. [10])					
Binary (Top number is value from cited source @25° C for comparison with p <sub>l</sub> )					
i	j	$\beta_{ij}^{(0)}$	$\beta_{ij}^{(1)}$	$C_{ij}^{\Phi}$	Applicability and/or Source
K <sup>+</sup>	Cl <sup>-</sup>	.04808 p <sub>1</sub> = 4.808E-02 p <sub>2</sub> = 1.0072E-02 p <sub>3</sub> = -7.58485E+02 p <sub>4</sub> = -4.7062E+00 p <sub>5</sub> = -3.7599E-06	0.21803 p <sub>1</sub> = 0.21717 p <sub>2</sub> = 5.2294E-02 p <sub>3</sub> = -2841.2582 p <sub>4</sub> = -21.01945 p <sub>5</sub> = -2.053E-05	-7.8800E-4 p <sub>1</sub> = -7.88E-04 p <sub>2</sub> = -1.29801E-03 p <sub>3</sub> = 91.2712 p <sub>4</sub> = 0.58645 p <sub>5</sub> = 4.95714E-07	273-523 K, I ≤ 18 m Greenberg & Moller (1989)
Na <sup>+</sup>	Cl <sup>-</sup>	0.0754 p <sub>1</sub> = 0.075375 p <sub>2</sub> = 0.10427 p <sub>3</sub> = -4339.3521 p <sub>4</sub> = -36.4314 p <sub>5</sub> = -5.0574E-05	0.2770 p <sub>1</sub> = 0.27709 p <sub>2</sub> = 0.23027 p <sub>3</sub> = -9070.0006 p <sub>4</sub> = -79.098 p <sub>5</sub> = -1.1085E-04	1.400E-03 p <sub>1</sub> = 1.396E-03 p <sub>2</sub> = -0.01789 p <sub>3</sub> = 714.8434 p <sub>4</sub> = 6.1419 p <sub>5</sub> = 8.7550E-06	273-373 K, I ≤ 6 m Pitzer et al. (1984) [Greenberg & Moller (1989) used it for I ≤ 18 m ]
Mixing					
i	j	k	θ <sub>ij</sub>	ψ <sub>ijk</sub>	
K <sup>+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	p <sub>1</sub> = -3.2035E-03 p <sub>3</sub> = 14.0213	p <sub>1</sub> = -3.6915E-03 p <sub>3</sub> = -5.10213	273-523, I ≤ 18 m Greenberg & Moller (1989)
Equilibrium Constants ( Values for Eq. [9])					
Dissociation Constant					
HCl ↔ H <sup>+</sup> + Cl <sup>-</sup>		A = 682.1261 B = -9466.866 C = -122.166 D = 0.20041		Van't Hoff expression used to extrapolate from Robinson's (1936) values at 0-50° C to 100° C, then the 0-100° C values were fitted to Eq. [9].	
Solubility Product					
KCl <sub>(s)</sub> ↔ K <sup>+</sup> + Cl <sup>-</sup>		A = -561.807 B = 12298.70 C = 101.061 D = -0.178325		Fitted from solubility data and smoothed values of predicted stoichiometric molal activity coefficients reported in Conceicao et al. (1983) for 10-120° C.	
NaCl <sub>(s)</sub> ↔ Na <sup>+</sup> + Cl <sup>-</sup>		A = 98.6399 B = -4549.03 C = -14.0476 D = 9.98306E-04		Fitted from solubility data and smoothed values of predicted stoichiometric molal activity coefficients reported in Pitzer et al. (1984) for 0-100° C.	



Table 19. Pitzer Parameters Regressed in This Work.

Values for Eq. [10]						
Binary	$\beta_{ij}^{(o)}$	$\beta_{ij}^{(1)}$	$C_{ij}^{\phi}$	$\lambda_{(n,i)} + \lambda_{(n,j)}$	$\lambda_{(n,n)}$	$6^* \mu_{(n,n,n)}$
Salt (n) i j						
HCl H <sup>+</sup> Cl <sup>-</sup>	p <sub>1</sub> = 0.182097 p <sub>2</sub> = -4.7855E-04	p <sub>1</sub> = 0.26949 p <sub>2</sub> = 1.15414E-03	p <sub>1</sub> = -5.2129E-04 p <sub>2</sub> = -6.07365E-06	p <sub>1</sub> = -0.14412 p <sub>2</sub> = 0.2174697 p <sub>3</sub> = -5.2425325E03 p <sub>4</sub> = -58.8492 p <sub>5</sub> = -1.286243E-04	p <sub>1</sub> = 1.33045 p <sub>2</sub> = 5.738129 p <sub>3</sub> = -2.20339704E05 p <sub>4</sub> = -1.969835E03 p <sub>5</sub> = -2.74204E-03	
HNO <sub>3</sub> H <sup>+</sup> NO <sub>3</sub> <sup>-</sup>	p <sub>1</sub> = 1.06748E-01 p <sub>2</sub> = -4.17059E-01 p <sub>3</sub> = 1.55697E+04 p <sub>4</sub> = 1.40743E+02 p <sub>5</sub> = 2.02044E-04	p <sub>1</sub> = 4.24077E-01 p <sub>2</sub> = 1.56612E+00 p <sub>3</sub> = -6.06191E+04 p <sub>4</sub> = -5.36308E+02 p <sub>5</sub> = -7.50816E-04	p <sub>1</sub> = 3.36204E-03 p <sub>2</sub> = 1.42854E-01 p <sub>3</sub> = -5.54797E+03 p <sub>4</sub> = -4.92530E+01 p <sub>5</sub> = -6.71937E-05	p <sub>1</sub> = 7.28705E-02 p <sub>2</sub> = -6.08708E-01 p <sub>3</sub> = 2.12602E+04 p <sub>4</sub> = 1.98048E+02 p <sub>5</sub> = 3.07216E-04	p <sub>1</sub> = 8.50979E-02 p <sub>2</sub> = 6.18657E-01 p <sub>3</sub> = -2.15945E+04 p <sub>4</sub> = -2.00533E+02 p <sub>5</sub> = -3.17230E-04	p <sub>1</sub> = -9.16286E-03 p <sub>2</sub> = -4.37071E-02 p <sub>3</sub> = 1.39539E+03 p <sub>4</sub> = 1.35373E+01 p <sub>5</sub> = 2.35023E-05
Mixing (Ionic)						
i j k	$\theta_{ij}$	$\psi_{ijk}$	Concentration & Temperature Range of Regressed Data			
H <sup>+</sup> K <sup>+</sup> Cl <sup>-</sup>	p <sub>1</sub> = 3.2863E-02 p <sub>3</sub> = 29.621	p <sub>1</sub> = -1.8449E-02 p <sub>3</sub> = -23.2078	273-323 K, I ≤ 17.5 m			
H <sup>+</sup> Na <sup>+</sup> Cl <sup>-</sup>	p <sub>1</sub> = 2.649E-02 p <sub>3</sub> = 33.508	p <sub>1</sub> = -2.7726E-04 p <sub>3</sub> = -8.4092	273-323 K, I ≤ 17.5 m			
Mixing (Involving Molecular HCl)						
i j	$\lambda_{(HCl,i)} + \lambda_{(HCl,j)}$	Concentration & Temperature Range of Regressed Data				
K <sup>+</sup> Cl <sup>-</sup>	p <sub>1</sub> = -3.0071E-02 p <sub>3</sub> = 1317.847	273-323 K, m ≤ 16				
Na <sup>+</sup> Cl <sup>-</sup>	p <sub>1</sub> = -7.14863E-01 p <sub>3</sub> = -601.411	273-323 K, I ≤ 17.5				
(The value of all other potential mixing parameters μ involving molecular HCl (such as μ <sub>(HCl,K<sup>+</sup>,Na<sup>+</sup>)</sub> and μ <sub>(HCl,HCl,Na<sup>+</sup>)</sub> ) were assumed negligible and set to zero.)						

Table 20. Equilibrium Constants Regressed in This Work.

Values for Eq. [9]	
<i>Dissociation Constant</i>	
$\text{HNO}_3 \leftrightarrow \text{H}^+ + \text{NO}_3^-$	A = -1.56132 B = 1325.9097
<i>Henry's Law Constant</i>	
$\text{HCl} \leftrightarrow \text{HCl}_{(\text{g})}$	A = 309.6451 B = -5570.5156 C = -57.0677 D = 0.126606
$\text{HNO}_3 \leftrightarrow \text{HNO}_{3(\text{g})}$	A = -1053.8932 B = 23382.0866 C = 183.816 D = -0.267282
$\text{HNO}_3 \leftrightarrow \text{HNO}_{3(\text{g})}$	A = -244.2011 B = 1293.3171 C = 43.19882 D = -0.0474445

Isothermal regressions of Perry & Green (1997) data.

Transformed CB (Determined from Eq. [A9] using Henry's law constant from Clegg & Brimblecombe (1990) assuming complete dissociation and the dissociation constant given in this table)

Table 21. Average Absolute Deviations Of Complete-Dissociation & Association-Based Approaches @25° C. \*

Data Sources	Data	Conc.	Modeling Approach		
			Association-Based †	Complete-Dissociation	
				Pitzer (1991) for $m \leq 6$ ‡	This work for $m \leq 16$ (HCl), 20 (HNO <sub>3</sub> )
<i>HCl-H<sub>2</sub>O</i>					
Hamer & Wu (1972), Robinson & Stokes (1959), Harned & Own (1958), Hawkins (1932), Partanen & Covington (2002), Cerquetti et al. (1968)	$\gamma_{\pm, \text{st}}$ (HCl)	$m \leq 6$	0.30%	0.39% N/A	1.30% 1.51%
		$m \leq 16$	0.41%		
	Robinson & Stokes (1959)	$\gamma_{\pm, \text{st}}$ (HCl) $\phi_{\text{st}}$	$m \leq 6$	0.31% 0.15%	0.43% 0.19%
Robinson & Stokes (1959), Hamer & Wu (1972)	$\phi_{\text{st}}$	$m \leq 6$	0.16%	0.17%	0.66%
		$m \leq 16$	0.19%	N/A	0.69%
<i>HNO<sub>3</sub>-H<sub>2</sub>O</i>					
Redlich et al. (1968), Hamer & Wu (1972)	$\gamma_{\pm, \text{st}}$ (HNO <sub>3</sub> )	$m \leq 6$	0.54%	0.36%	1.17%
		$m \leq 20$	0.51%	N/A	1.25%
Hamer & Wu (1972)	$\gamma_{\pm, \text{st}}$ (HNO <sub>3</sub> )	$m \leq 6$	0.43% (0.35%)	0.19%	1.01%
		$m \leq 20$	0.44% (0.34%)	N/A	1.15%
	$\phi_{\text{st}}$	$m \leq 6$	0.35% (0.28%)	0.09%	0.60%
		$m \leq 20$	0.32% (0.26%)	N/A	0.74%

\* See notes to Tbl. 22 for definition of average absolute deviation.

† Multi-temperature parameterization given in Tbls. 18-20. Values in parenthesis, however, correspond to an isothermal regression of HNO<sub>3</sub> activity coefficient, osmotic coefficient, and dissociation data, where the activity coefficient data was limited to that of Hamer & Wu (1972).

\*  $\beta_{(H^+, Cl^-)}^{(o)} = 0.1775$ ,  $\beta_{(H^+, Cl^-)}^{(i)} = .2945$ ,  $C_{(H^+, Cl^-)}^{\Phi} = 0.0080$ ;  $\beta_{(H^+, NO_3^-)}^{(o)} = 0.1168$ ,  $\beta_{(H^+, NO_3^-)}^{(i)} = 0.3546$ ,  $C_{(H^+, NO_3^-)}^{\Phi} = -0.00539$ .

Table 22. Summary of Results: Average Absolute Deviation Between Predicted And Experimental Values.\*

Aqueous System	$\gamma_{\pm, \text{st}}$	$\phi_{\text{st}}$	VLE	SLE	$\alpha$
HCl	(0-50°, 0 < m ≤ 16; 60-110°, 0 < m ≤ 7) 0.6% (5-55°, 0 < m ≤ 4) <b>0.24%</b> (70-80°, 7 < m ≤ 11) <b>4.5%</b>	0.3% (25, 60-110°)	(p <sub>HCl</sub> : 0-50°) 2.05% (p <sub>HCl</sub> : 60-110°) 4.41% (p <sub>HCl</sub> : 0-110°) 2.70% ** (p <sub>Total</sub> : 50-121°, 1 < m ≤ 13.5) <b>1.36%</b>	N/A	
HCl-NaCl	(0-50°, 0 < I ≤ 3 m, $\gamma_{\pm, \text{st(HCl)}}$ ) 0.42% † (25°, 0 < I ≤ 7 m, $\gamma_{\pm, \text{st(HCl)}}$ ) 1.44%	N/A	N/A	(0-30°, 6 ≤ I ≤ 17.5 m) 4.92% † (25°, 6 ≤ I ≤ 19 m) 4.21%	N/A
HCl-KCl	(0-50°, 0 < I ≤ 3.5 m, $\gamma_{\pm, \text{st(HCl)}}$ ) 1.06% (25°, 0 < I ≤ 5 m, $\gamma_{\pm, \text{st(HCl)}}$ ) 1.28% (5-45°, 0 < I ≤ 1.5 m, $\gamma_{\pm, \text{st(HCl)}}$ ) <b>0.60%</b> ‡	N/A	N/A	(0°, 3.8 ≤ I ≤ 17.4 m) 6.42% (0°, 19 ≤ I ≤ 20.8 m) <b>4.21%</b> (25°, 5 ≤ I ≤ 16 m) 2.02% (25°, I = 17.6 m) <b>0.64%</b>	
HCl-KCl-NaCl @ 25°	(4 ≤ I ≤ 6 m) 3.12%	N/A	(p <sub>HCl</sub> : I = 5 m) <b>5.64%</b>	(7 ≤ I ≤ 14 m) 6.08%	
HNO <sub>3</sub>	(25°) 0.51% (Clegg & Brimblecombe "input" 0-110°) 0.14% †	0.32% (25°)	Transformed CB Isothermal Regression p <sub>HNO3</sub> : Perry & Green (1997) 5-120°, 4-24 m <b>19.3%</b> 14.0% p <sub>HNO3</sub> : Ellis & Thwaites (1957) 106-117°, 6-20 m <b>25.2%</b> <b>14.8%</b>	N/A	(0, 25 & 70°) 1.43% (0 & 50°) <b>3.45%</b>

\* Unless stated otherwise, the ionic strength and temperature ranges are 0-16 m: 0-110° C (chloride systems) and 0-20 molal: 0-120° C (HNO<sub>3</sub>). Shaded averages indicate that the corresponding data was not used to regress model parameters. Absolute deviation = |data-predicted|/data. Average absolute deviation =

$$\sum_i^n \frac{|data_i - predicted_i|}{data_i} \quad \text{where the summation is over all data points } i, \text{ and } n \text{ is the number of data points. Deviations given in terms of percentages are merely multiplied by one hundred. For solubility data, } data_i \text{ and } predicted_i \text{ refer to the thermodynamic solubility product and the predicted ionic product at saturation, respectively.}$$

\*\* Total average for two previous cell entries at 0-50° and 60-110° C.

† Excludes data at 25° C.

‡ Data is distinct from that of other entries in the cell.

Table 23. Data Used To Regress Equilibrium Constants & Pitzer Parameters.

Data Source	No. Points Used	Data Type	Average Abs. Dev.	T (C)	Concentration
<i>HNO<sub>3</sub>-H<sub>2</sub>O System Parameterization</i>					
Krawetz (1955)	14	$\alpha$	1.43%	25	0.9-20.1
Davis & De Bruin (1964)	29	$\alpha$	0.49%	25	0.005-20.6
Hood & Reilly (1960)	24	$\alpha$	2.56%	0, 25, 70	1.0-20.7
Hamer & Wu (1972)	43	$\gamma_{\pm, \text{st}}(\text{HNO}_3)$ $\phi_{\text{st}}$	0.44% 0.32%	25	0.001-20.0
Redlich et al. (1968)	12	$\gamma_{\pm, \text{st}}(\text{HNO}_3)$	0.77%	25	0.001-10.6
Clegg & Brimblecombe (1990)	689	model $\Rightarrow \gamma_{\pm, \text{st}}(\text{HNO}_3)$	0.14%	0-110	0.005-20.0
Perry & Green (1997; appears to be same as I.C.T.)	116	$P_{\text{HNO}_3}$	14.00% *	5-120	4.0-23.8
<i>HCl-H<sub>2</sub>O System Parameterization</i>					
Holmes et al. (1987)	57	model $\Rightarrow \gamma_{\pm, \text{st}}(\text{HCl})$ model $\Rightarrow \phi_{\text{st}}$	0.24% 0.14%	90-110	0.10-7
Perry & Green (1997; appears to be same as I.C.T.)	50	$P_{\text{HCl}}$ $P_{\text{H}_2\text{O}} \Rightarrow \phi_{\text{st}}$	4.41% 0.65%	60-110	6.0-15.4 8.7-16.8
Fritz & Fuget (1956)	125	$P_{\text{HCl}}$	2.05%	0-50	0.01-15.9
Hamer & Wu (1972)	39	$\gamma_{\pm, \text{st}}(\text{HCl})$ $\phi_{\text{st}}$	0.45% 0.21%	25	0.001-16
Robinson & Stokes (1959)	23	$\gamma_{\pm, \text{st}}(\text{HCl})$ $\phi_{\text{st}}$	0.31% 0.15%	25	0.1-6.0
Akerlof & Teare (1937)	84	$\gamma_{\pm, \text{st}}(\text{HCl})$	0.98%	0-50	3.0-6.0
Cerquetti et al. (1968)	50	$\gamma_{\pm, \text{st}}(\text{HCl})$	1.03%	25-60	1-11.1
	12		0.48%	70 & 80	1-6.9
	1		0.77%	90	1.0
	63		0.92%		
Harned & Owen (1958)	96	$\gamma_{\pm, \text{st}}(\text{HCl})$	0.20%	0, 10, 20, 25, 30, 40, 50, 60	0.002-2.0
Hawkins (1932)	3	$\gamma_{\pm, \text{st}}(\text{HCl})$	0.33%	25	1.0-4.0
Macaskill et al. (1977)	12	$\gamma_{\pm, \text{st}}(\text{HCl})$	0.44%	10, 20, 30, 40	0.4-0.9
Partanen & Covington (2002)	8	$\gamma_{\pm, \text{st}}(\text{HCl})$	0.04%	0, 10, 20, 25, 30, 40, 50, 60	0.01

Table 23 (Continued). Data Used To Regress Equilibrium Constants & Pitzer Parameters.

Parameterization of Chloride Mixtures **									
HCl-KCl-H <sub>2</sub> O System					Ionic Strength (mol/kg)		HCl Ionic Strength Fraction		
Linke & Seidell (1965)	19	SLE <sub>KCl</sub>	6.42%	0	3.8-17.4	0.18-0.99 0.15-0.98			
	<u>18</u> 37		<u>2.02%</u> 4.28%	25	5-16				
Harned & Owen (1958)	131	$\gamma_{\pm, st}(HCl)$	1.06%	0-50	0.02-3.5	0.003-0.5			
Hawkins (1932)	19	$\gamma_{\pm, st}(HCl)$	2.01%	25	0.1-5.0	0.003-0.8			
Macaskill & Bates (1978)	35	$emf \Rightarrow \gamma_{\pm, st}(HCl)$	0.96%	25	0.1-3.0	0.1-0.9			
HCl-NaCl-H <sub>2</sub> O System									
Linke & Seidell (1965)	13	SLE <sub>NaCl</sub>	3.21%	0	5.9-17.6	0.02-0.99			
	8		3.99%	18	5.9-6.3	0.01-0.72			
	17		4.21%	25	6.1-19.0	0.04-0.999			
	<u>12</u> 50		<u>7.40%</u> 4.68%	30	6.0-15.2	0.09-0.998			
	99		0.41%	0-50	0.02-3.0	0.004-0.5			
Harned & Owen (1958)	28	$\gamma_{\pm, st}(HCl)$	1.56%	25	0.1-6.0	0.003-0.83			
Hawkins (1932)	19	$emf \Rightarrow \gamma_{\pm, st}(HCl)$	0.29%	25	0.1-0.87	0.1-0.9			
Macaskill et al. (1977)	28	$\gamma_{\pm, st}(HCl)$	2.44%	25	4.0-7.0	0.1-0.9			
Jiang (1996a)									
HCl-KCl-NaCl-H <sub>2</sub> O System									
Jiang (1996b)	27	$\gamma_{\pm, st}(HCl)$	3.12%	25	4.0-6.0	0.08-0.72			
Linke & Seidell (1965)	4	SLE <sub>KCl</sub>	5.57%	25	7.1-14.0	0.45-0.98			0.003-0.035
		<u>SLE<sub>NaCl</sub></u> SLE	<u>6.60%</u> 6.08%						

See notes to Tbl. 22 for definition of average percent absolute deviation.

\* Using temperature-dependent correlation for Henry's law constant determined from isothermal regressions of VLE data.

\*\* Ionic strength and its fractions are stoichiometric (calculated assuming complete dissociation).

Table 24. Data Used To Validate, But Not Regress, Model Parameters.

Data Source	No. Points Used	Data Type	Average Abs. Dev.	T (C)	Concentration
HNO <sub>3</sub> -H <sub>2</sub> O System Parameterization					
Krawetz (1955)	5	α	3.61%	0	1.6-19.1
	15		3.39%	50	0.9-20.0
	20		3.45%		
Ellis & Thwaites (1957)	7	P <sub>HNO3</sub>	14.75% *	106-117	5.9-20.1
HCl-H <sub>2</sub> O System Parameterization					
Sako et al. (1984)	10	P <sub>HCl</sub>	17.02%	101-108.6	1.3-8.4
Sako et al. (1985)	21	P <sub>Total</sub>	1.36%	50-121	1.3-13.4
Cerquetti et al. (1968)	8	γ <sub>±, st (HCl)</sub>	4.48%	70 & 80	7.9-11.1
Harned & Owen (1958)	59	γ <sub>±, st (HCl)</sub>	0.21%	5, 15, 35, 45, 55	0.002-2.0
Macaskill et al. (1977)	12	γ <sub>±, st (HCl)</sub>	0.48%	5, 15, 35, 45	0.4-0.9
Partanen & Covington (2002)	5	γ <sub>±, st (HCl)</sub>	0.04%	5, 15, 35, 45, 55	0.01
HCl-KCl-H <sub>2</sub> O System Parameterization **					
Macaskill et al. (1978)	239	emf ⇒ γ <sub>±, st (HCl)</sub>	0.60%	5-45	0-1.5
Linke & Seidell (1965)	2	SLE <sub>KCl</sub>	4.21%	0	19.0-20.8
	1		0.64%	25	17.6
	3		3.02%		0.98
HCl-KCl-NaCl-H <sub>2</sub> O System Parameterization **					
Clegg & Brimblecombe (1988b)	6	P <sub>HCl</sub>	5.64%	25	5.0
					0-7

See notes to Tbl. 22 for definition of average % absolute deviation.

\* Using temperature-dependent correlation for Henry's law constant determined from isothermal regressions of VLE data.

\*\* Ionic strength and its fractions are stoichiometric (calculated assuming complete dissociation).